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RSIC-381

SILICON CARBIDE FOR SEMICONDUCTORS

by
Gus J. Caras

February 1965

Redstone Scientific Information Center

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by

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ABSTRACT

This state-of-the-art survey on silicon carbide for semiconductors includes a bibliography of the most important references published as of the end of 1964. The various methods used for growing silicon carbide single crystals are reviewed, as well as their properties and devices fabricated from them. The fact that the state-of-the-art of silicon carbide semiconductors is not further advanced may be attributed to the difficulties of growing single crystals of sufficient size and purity for semiconductor applications. Of the various methods of growing silicon carbide, growth by sublimation appears to be the most successful method. There is considerable variation in the properties of silicon carbide as reported in the literature, mainly because most measurements were conducted on crystals with varying amounts and types of impurities. In the area of devices, rectifiers capable of 500°C operation and unipolar transistors exhibiting power gain at temperatures greater than 500°C have been fabricated. Other devices which have received attention include diodes, photoelectric and electroluminescent devices, and electron emission components.

FOREWORD

This state-of-the-art survey summarizes the most important information found in the published literature concerning silicon carbide. Although emphasis was placed on covering the literature published since January 1961, there are several instances where older literature was reviewed, either because of the lack of newer material in certain areas, or because some of these older references were considered significant and contributed in the preparation of this survey. Only the type of silicon carbide which is suitable for the fabrication of semiconductor devices was considered. This type is of relatively high purity and in single crystal form as opposed to commercial silicon carbide which is used mainly as a refractive and abrasive material.

The information for this survey was taken from the information sources available at the Redstone Scientific Information Center (RSIC), which include the following:

1. RSIC holdings (books, reports, and journals).
2. NASA (a computer tape search of NASA tapes which contain references from the Scientific and Technical Aerospace Reports, and the International Aerospace Abstracts).
3. Defense Documentation Center (DDC) (Pertinent references including abstracts furnished by the Defense Documentation Center, Arlington 12, Virginia).

In addition, references to the patent literature were obtained from the patent holdings of the Price Gilbert Library, Georgia Institute of Technology, Atlanta, Georgia.

The survey is divided into two main parts. The first part consists of a summary based on a review of pertinent literature, while the second part consists of a bibliography in which nearly all of the references are accompanied by abstracts. The entries in the bibliography are arranged in alphabetical order by corporate source or personal author. The corporate source is used in listing technical reports, which are normally considered company or organization documents. The personal authors are used for articles published in journals, books, etc. This arrangement should not present any difficulties in using the bibliography since a personal author index is also included. It was not very convenient to subdivide the bibliography by subject matter since a large number of references dealt with more than one topic. In lieu of such subdivision,

a subject index is provided. Since most of the research on silicon carbide was conducted under various government contracts, it was considered advantageous to include a contract number index.

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Section I. INTRODUCTION

Silicon carbide, SiC, is a crystalline material varying in color from pale green to black, depending upon the amount of impurities. It was first prepared by E. G. Acheson in 1891 by heating a mixture of carbon and clay to about 2000°C in the electric furnace. Because of its extreme hardness (only diamond and boron carbide are harder) and stability up to very high temperatures, its main uses have been as an abrasive and refractory material.

The semiconducting properties of electronic grade crystals of silicon carbide make this material potentially extremely useful in the field of semiconductors, particularly for some military and space applications. Devices fabricated from such a material can operate successfully in a high temperature and radiation environment. For this reason, considerable research has been conducted, mostly sponsored by Federal agencies, in an effort to obtain silicon carbide crystals of the proper size and purity for semiconductor applications.

Polycrystalline SiC varistors have been produced commercially for some time, but devices requiring the use of single crystals have been developed rather slowly. Silicon carbide is difficult to grow, shape, and etch and, although the technological understanding of other semiconductors has contributed to the development of silicon carbide, new techniques may need to be developed before SiC devices can be reliably produced.

Silicon carbide can crystallize in two basic forms, cubic and hexagonal. The cubic form, called β -SiC, may be formed by reacting silicon and carbon at temperatures below 2000°C. The hexagonal form has at least six variations of its basic structure, designated α -I, II, III, IV, V, and VI and is formed in the temperature range of 2400° to 2600°C.

Section II. GROWTH OF SILICON CARBIDE CRYSTALS

1. The Silicon Carbide Binary System

Before one can synthesize a compound efficiently, the effects of pressure and temperature on its composition must be determined. The temperature-composition diagram for SiC is shown in Figure 1. The only condensed phases that occur in this binary system are silicon, silicon carbide, and graphite. The solubility of carbon in liquid silicon is very slow at the melting point of silicon but increases progressively with temperature and reaches one atomic percent at 2150°C.^{1, 2}

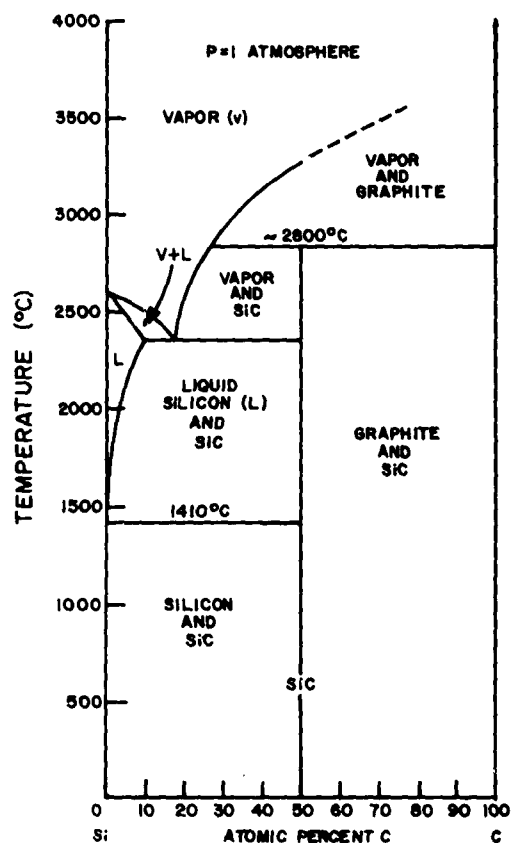


Figure 1. Temperature-Composition Phase Diagram

Above 2800°C a peritectic transformation occurs in which SiC decomposes into graphite and silicon-rich vapor. In studying the phase relationships in this system, the pressure parameter must also be considered. The phase diagram should be visualized as a prismatic body with three axes representing composition, temperature, and pressure. One isothermal section of such a phase diagram constructed by Smiltens is shown in Figure 2. At some elevated pressure the distance A-B vanishes and a theoretical quadruple point at which vapor, liquid silicon, silicon carbide, and graphite are in equilibrium is reached.³

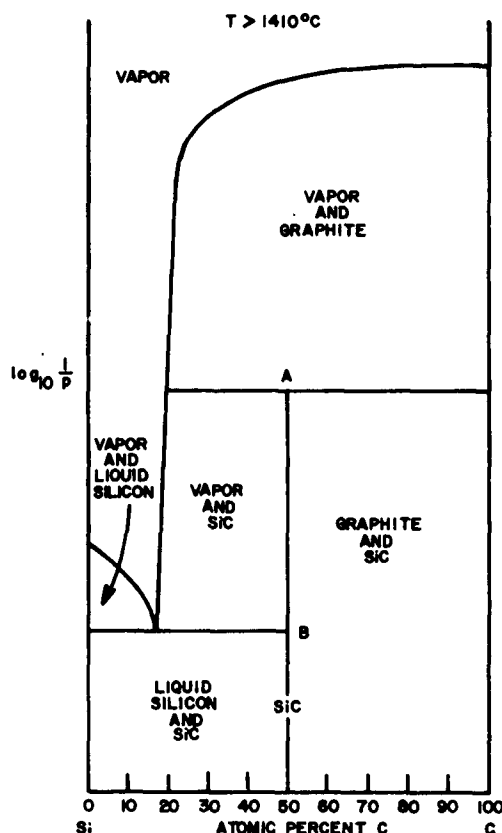


Figure 2. Isothermal Section of a Pressure-Composition Phase Diagram

Scace and Slack⁴ studied the solubility of carbon in liquid silicon at elevated temperatures and pressures in the furnace shown in Figure 3. The vessel held a pressure as high as 1000 psi, which retarded the evaporation of silicon. All parts were made of graphite. The two current terminals supported a tubular heater, two radiation shields, and a container that was used in the experiments on the solubility of carbon in silicon. The assembly could be heated to approximately 3500°C. Optical pyrometry was used to measure temperatures. In order to determine the solubility of carbon in silicon, the inner container was filled with silicon, sealed tightly, and heated to a temperature between 2100° and 2900°C. Thermal equilibrium was achieved quite rapidly, and the sample was held at a fixed temperature for 1 or 2 minutes, after which the power was shut off. Then the furnace temperature decreased quite rapidly, through radiation cooling, and the silicon froze.

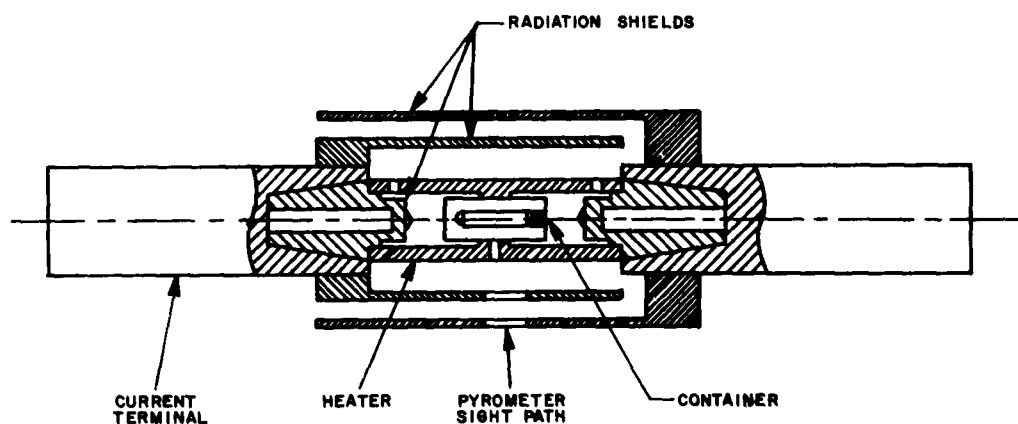


Figure 3. The High-Temperature Solubility Apparatus of Scace and Slack

The solubilities obtained are summarized in Figure 4. Of particular interest are the solubilities of carbon in liquid silicon at the silicon melting point, 5×10^{-3} atomic percent (5×10^{17} c/cm³ Si), and at the decomposition temperature of 2830°C. This is the maximum temperature at which silicon carbide could be grown from a silicon solution, and the carbon content of the melt here is 19 atomic percent. This high solubility indicated that growth from solution is feasible. The vapor pressure of silicon over liquid silicon and over SiC at this temperature is of the order of one atmosphere and rising rapidly;

therefore, the need for a pressurized atmosphere to maintain stable conditions is apparent. Another method for plotting the data obtained by Scace and Slack is on a temperature versus composition phase diagram as shown in Figure 5. Here the behavior of SiC at the decomposition temperature may be clearly seen.²

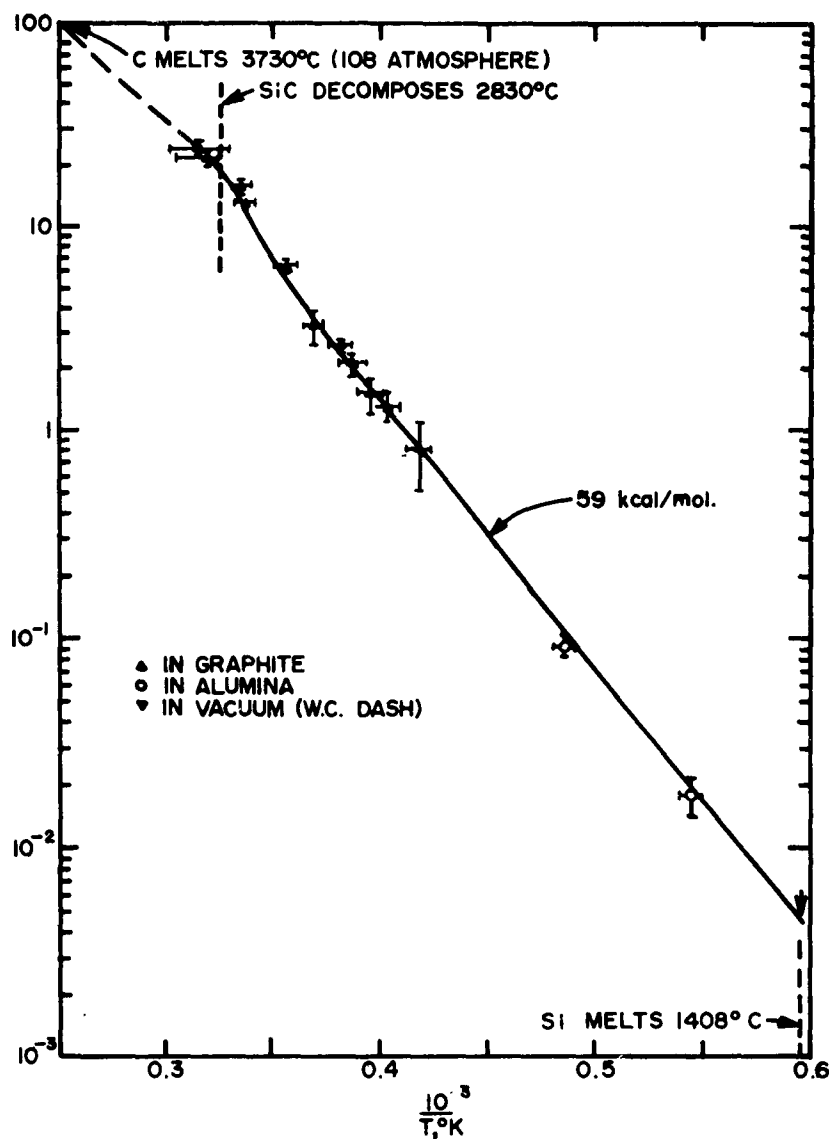


Figure 4. Solubility (Atomic Percent) of Carbon in Liquid Silicon as a Function of Reciprocal Temperature

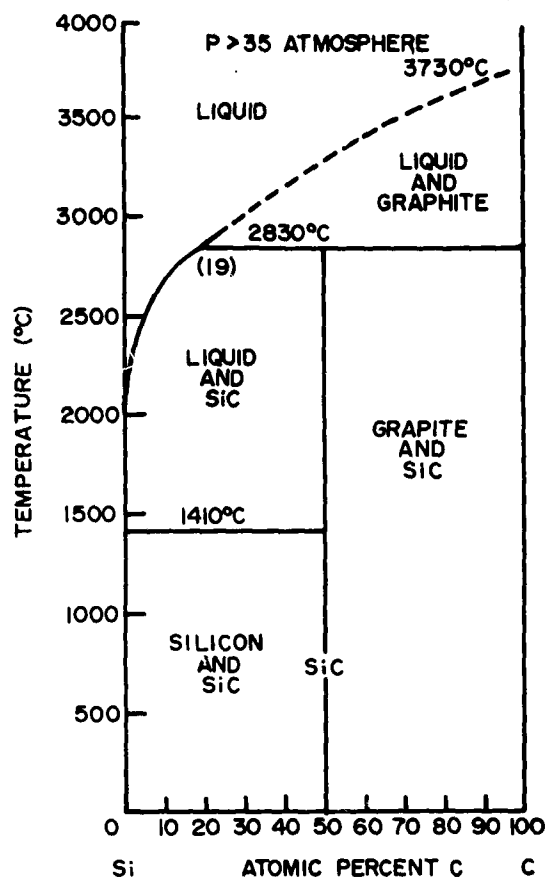


Figure 5. Temperature-Composition Phase Diagram

2. Crystal Growth Mechanisms

The general theories of crystal growth distinguish between two major mechanisms: (1) the surface advances by the lateral motion of steps, or (2) the growth interface advances normal to itself without steps. The actual mechanism depends on the nature of the surface. For a surface in which the change from one phase to the other is gradual, crystal growth occurs normal to the interface. In other words, the interface advances normal to itself without the need for steps. For an interface for which the surface tension as a function of orientation has a sharp minimum, the interface requires steps in order to advance normal to itself.⁵

The crystals of hexagonal types (the α -forms) are usually in the form of thin platelets, the faces of which are singular (0001) planes. The edges of the plates are composed of (21 $\bar{3}$ 0) planes. In addition, the (0001) planes are smooth, but the edges must be atomically rough because the stacking faults act as low-energy twin boundaries. Each

twin plane will introduce one reentrant corner on these faces. Therefore, with α -SiC, both types of crystal growth are operative; on the smooth (0001) planes, steps are necessary for growth, whereas the edges of these crystals can readily advance normal to themselves into regions of supersaturated vapors.²

The steps can form by classical two-dimensional nucleation if

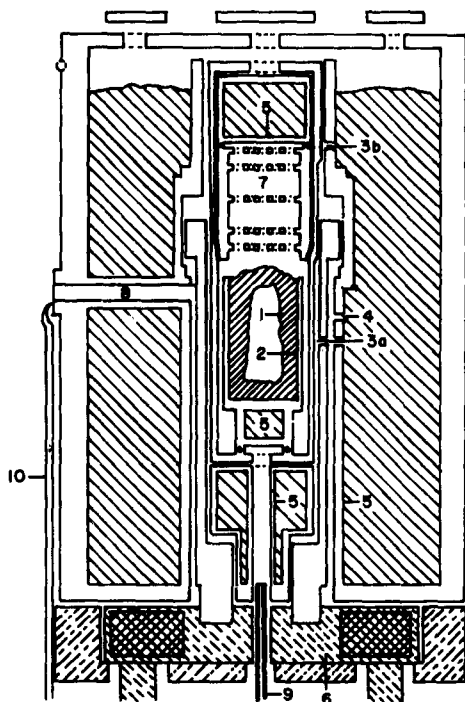
$$\pi d^2 \sigma < 50kT$$

where d is the step height and σ the surface free energy. If the minimum values of $d = 10\text{\AA}$ and $\sigma = 3000 \text{ ergs/cm}^2$ are used, it is obvious that the inequality is not true for temperatures as high as 2800°C . However, Amelinckx⁶ has reported that steps can be observed in all sizeable α -SiC crystals and that these steps are the results of operative screw dislocations during crystal growth. The conclusion is that growth normal to the (0001) faces proceeds by screw dislocations.

The growth of cubic SiC (the β forms) should be similar to that of other zinc-blende semiconductors such as Ge and Si. In recent studies of Ge grown from the melt, it appears that (211) planes are diffuse, whereas (111) planes are singular. Steps are normally required for growth on (111) planes. With Ge, however, the surface free energy is substantially reduced by the liquid to approximately 100 ergs/cm^2 , so that two-dimensional nucleations are feasible. These facts probably explain why β -SiC is grown more easily from solution than from the vapor.²

3. Growth by Sublimation

The most extensive published work on the preparation of single crystals of SiC by sublimation is that of Lely. He used commercial SiC as a starting material to grow single crystals from the vapor phase using the furnace shown in Figure 6. In Lely's furnace, as in commercial furnaces, crystals are grown inside cavities formed in bulk SiC but with much greater precision and control. The crystals are grown from SiC vapor, which sublimates and supersaturates the interior of the cavity. Nucleation occurs on the inner wall. Vapor pressure in the cavity is maintained by virtue of the constant decomposition of charge material at a temperature greater than that of the cavity; an equilibrium vapor pressure of the sort normally assumed in closed systems does not exist.



(1) SiC for sublimation; (2) graphite crucible; (3) graphite crucible made of two parts for protection of SiC; (4) heating element, a graphite tube split three-fourths of its length; (5) insulating body made with graphite lampblack; (6) water-cooled copper electrodes; (7) graphite network; (8) tube for pyrometer; (9) tube for introducing protective gas; (10) protective gas inlet. The furnace is surrounded by a water-cooled vacuum-type envelope.

Figure 6. Sublimation Furnace

In such a system, the maintenance of vapor pressure can be improved by making the charge material as dense as possible, but there are very serious practical limitations to this approach. For the most part, little can be done beyond careful preparation of the charge to ensure maximum density and homogeneity. Since crystal growth depends on the ability of the crystal to dissipate the heat of vaporization of the incoming molecules or atoms, temperature and, particularly, temperature gradients are very important, since these constitute the only controllable parameters in the growth process.²

Hamilton⁷ used a furnace similar to that of Lely, but capable of more precise temperature control. Radiation from a selected area of the heater is sensed by a thermopile which is arranged to adjust the power input to the furnace by means of a saturable core reactor. Short-term control is about $\pm 1^\circ\text{C}$ and this system is capable of maintaining constant temperatures for several hours. The furnace may be operated in high vacuum at temperatures up to 2000°C . Above this temperature, an inert gas such as argon is used to suppress evaporation of the graphite furnace components.⁸

An ideal condition for crystal growth by this process is shown in Figure 7. In this sketch, the dotted lines indicate the flow lines of the SiC vapor in the charge, and therefore are normal to the isotherms. The heavy black lines in the middle of the sketch represent the thin-walled graphite substrate. The lines radiating out from this substrate represent growing SiC crystals. The optimum growth conditions occur when the temperature at the side of the substrate is slightly higher than the temperatures at the top and bottom of the substrate. This serves as a radiation sink for the cavity. Inside the substrate cavity, the temperature should be somewhat lower, so that growth can occur. The middle third of the substrate should be of uniform temperature. If these conditions are not fulfilled, one or several of the following may be obtained: (1) Crystals may not grow perpendicular to the substrate, and stepped crystals will be produced, (2) many nucleation centers will be present and the crystals will be intergrown, (3) insufficient vapor source or opportunity for the growing crystals to radiate heat will result in small crystals, and (4) few nucleation centers at the proper portion of the substrate will result.⁹

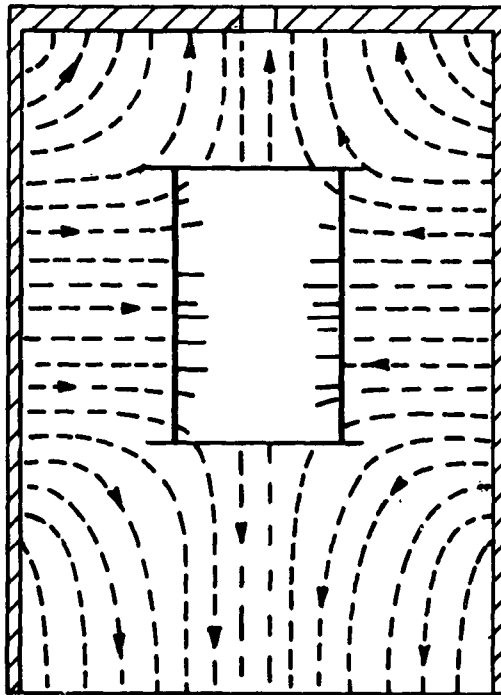


Figure 7. Cross Section of the Crucible

An example of conditions which lead to stepped crystal is shown in Figure 8. In this case, the temperature in the direction of growth (T_3) is much lower than T_1 or T_2 . Since this large difference exists, growth will proceed only in the downward direction and the crystal will tend to be stepped. Thus, it is extremely important that the temperature and temperature gradient be known and controlled.

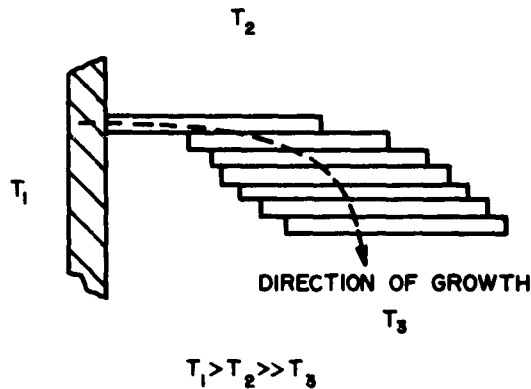


Figure 8. Stepped Crystal Growth

To effect greater control over the temperature and purity, a new Kroll-type furnace has been designed and built by the Westinghouse Electric Corporation.¹⁰ The most important features of the furnace are shown in Figure 9. The graphite and molybdenum shielding systems are designed to permit operation of the furnace at temperatures in excess of 2500°C with a minimum of powdered carbon insulation, a fact which will tend to reduce furnace contamination. The powdered carbon particles are on the order of 1 to 10 microns in diameter and thus a layer of this powdered carbon has a large surface area that can absorb nitrogen and other gases. In practice this layer is outgassed at about 1200°C. The new furnace has provisions for moving the charge out of the hot region so that high-temperature outgassing can take place without crystal growth. An exhaust system is provided to pump out the gaseous impurities before they condense on some cooler portion of the furnace. Other improvements of this furnace include one auxiliary heater for intensification of temperature gradients, and fractionating pump permitting both rapid evacuation of the furnace and a low ultimate pressure.^{10, 11, 12}

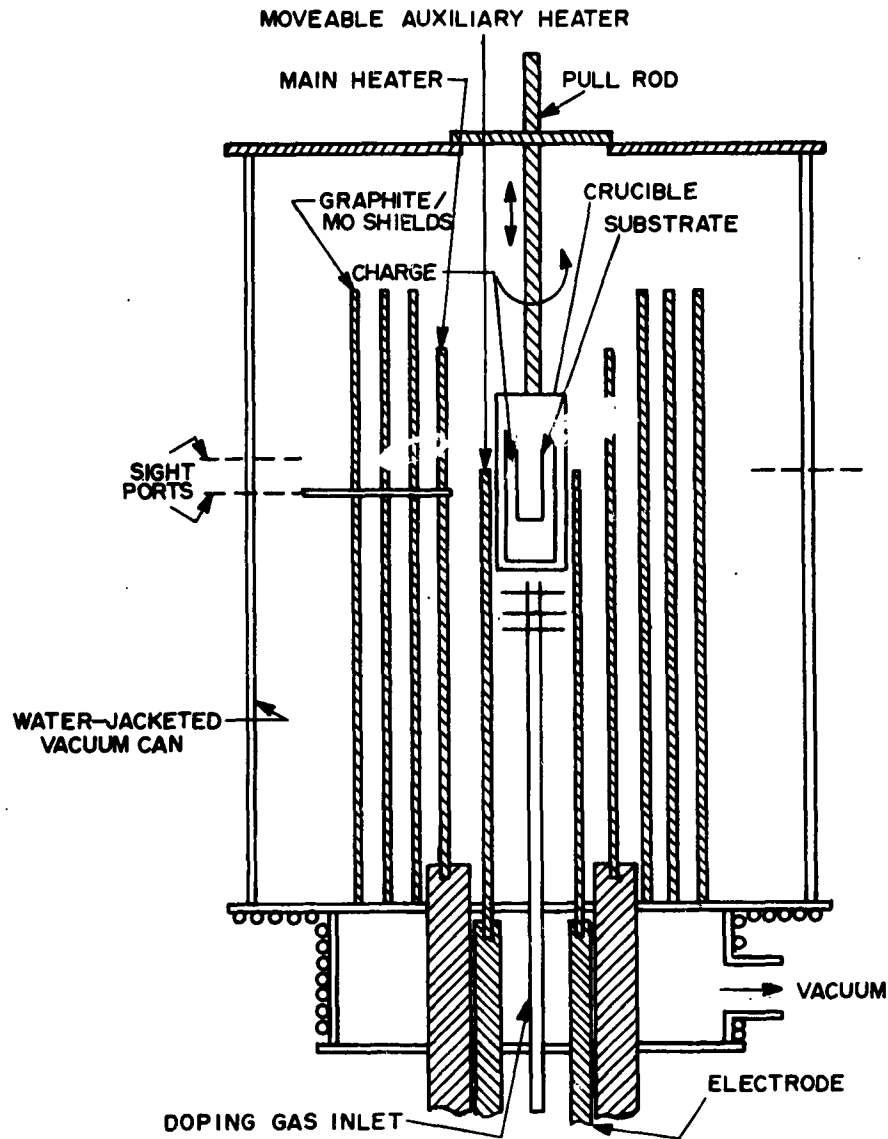


Figure 9. Improved High-Temperature Graphite Furnace

Westinghouse studied the growth of SiC crystals quite extensively under contracts AF 33(657)-8719 and AF 33(657)-7027. In spite of the modifications to the Kroll-type furnace, the yield of suitable crystals for device fabrication was low. The average yield from each preparation in a laboratory-type furnace was about 50 crystals which measured at least 2 millimeters or larger across the platelet face diagonal. About one-fourth of these crystals were large enough and had sufficient crystal perfection to be considered useful for further study. A minimum platelet size of about 4 millimeters is necessary for 1-ampere device fabrication, although smaller crystals can be used for lower rated devices.¹³

4. Growth by Gaseous Cracking

Kendall¹⁴ has shown that SiC crystals can be grown by gaseous cracking in the apparatus shown in Figure 10. By flowing mixtures of silicon tetrachloride, toluene, and hydrogen past a hot (2000°C) graphite filament, β -SiC crystals were grown. A number of compounds have been tried, but the most success has been obtained with a mixture of silicon tetrachloride and toluene.

Experiments have been performed by Merz¹⁵ using $\text{SiCl}_4 + \text{C}_7\text{H}_8 + \text{H}_2$ and $\text{CH}_3\text{SiCl}_3 + \text{H}_2$ in an inductively heated tube-furnace. The reaction tube was insulated with $1\frac{3}{4}$ inches of 1000-mesh SiC for temperatures below 2100°C. A quartz container held the insulation in place and supported the induction coil. The ends of the quartz cylinder were closed by end plates held in place by water-cooled copper bands bolted to the reaction tube. Water-cooled copper caps were sealed to the end of the reaction tube with Gooch crucible tubing. The caps were provided with two inlet tubes and a sight glass that allowed temperature measurement and control. A graphite tube supported the crucible and provided a sight path for the radiation pyrometer. A purging gas was fed into this tube to keep the sight path free of smoke. The crucible was 5 inches long and contained three evenly-spaced graphite sight rods that projected into the gas stream to provide means for temperature measurements at various positions along the crucible. The reaction gases were fed into the open top of the crucible and passed out through the holes in the crucible support plate, which also served as a cap for the crucible support tube. To remove HCl and SiCl_4 , the reaction and purge gases were exhausted into gas-washing bottles containing aqueous NaOH. The graphite tube furnace constructed by Merz is shown in Figure 11.

A typical temperature profile measured from top to bottom of the crucible was 1400°, 1600°, 1730°, and 1550°C at four equally spaced positions. The temperature was controlled by a proportioning control system coupled to phase-shifting rectifiers in a 400-kilocycle induction generator. The sensing element was a radiation pyrometer. The control equipment maintained the temperature constant within $\pm 10^\circ\text{C}$ at 1750°C. The carrier gas H_2 was bubbled through the liquid SiCl_4 and toluene at measured rates that were varied to provide definite Si/C ratios. The bubbling bottles were weighed before and after each run to determine consumption.

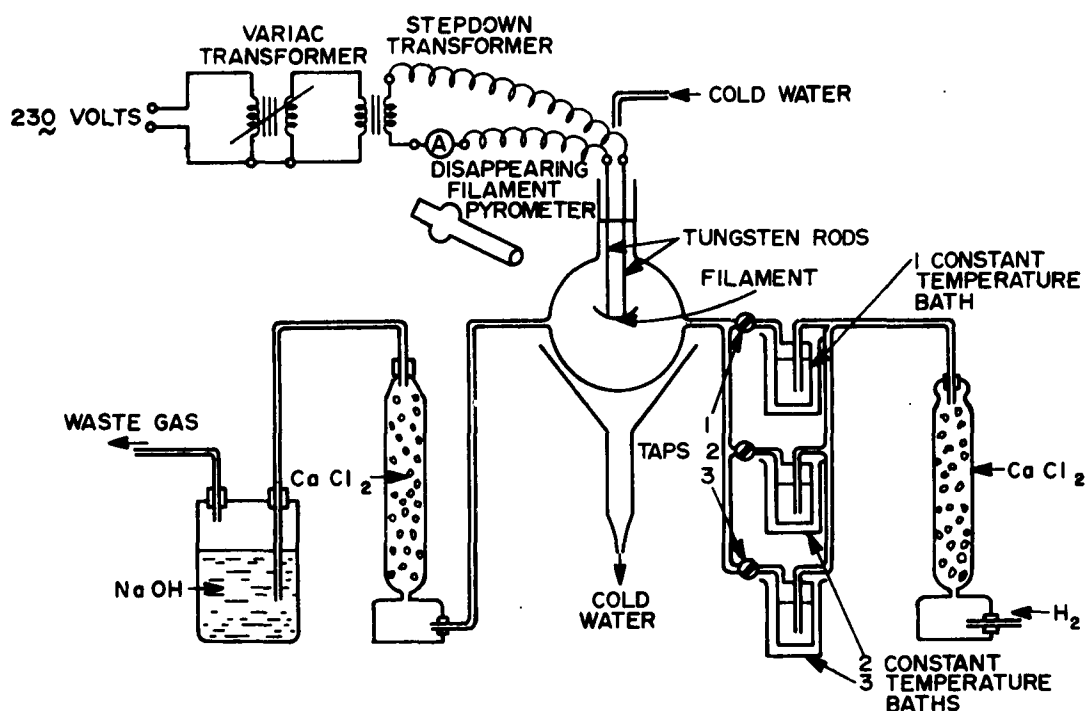


Figure 10. Kendall's Gaseous Cracking Apparatus

For experiments in the temperature range 2000° to 2500°C , a carbon resistance furnace with a 3-inch diameter tube was used. A dense graphite tube of 2-inch diameter and 7-foot length was placed inside the furnace tube with protruding ends. This reaction tube was capped as shown in Figure 11.

Experiments below 1500°C were done in a $1\frac{1}{4}$ -inch alumina tube furnace heated by SiC elements. The ends of the alumina tube were closed with rubber stoppers provided with inlet-outlet tubes and sight glasses. The chlorinated reagents used in this investigation, such as SiCl_4 and CCl_4 , were found to react with the alumina tube at temperatures greater than 1300°C . Hence both aluminum and oxygen must be considered part of the reaction system in these experiments.

Attempts were made to grow β -SiC crystals at 1450° to 2500°C from a mixture of SiCl_4 , C_7H_8 , and H_2 . Crystal growth did occur at 1600° to 2250°C , but below 1750°C the growth rate was quite slow. At 1750°C , the fastest growth was observed with a nominal Si/C ratio of 1 to 4 and 90 to 98.7 mole percent H_2 . The true Si/C ratio at the point of reaction was unknown since the H_2 reacted somewhat with the furnace interior. The gas velocity varied from 40 to 280 centimeters per minute.

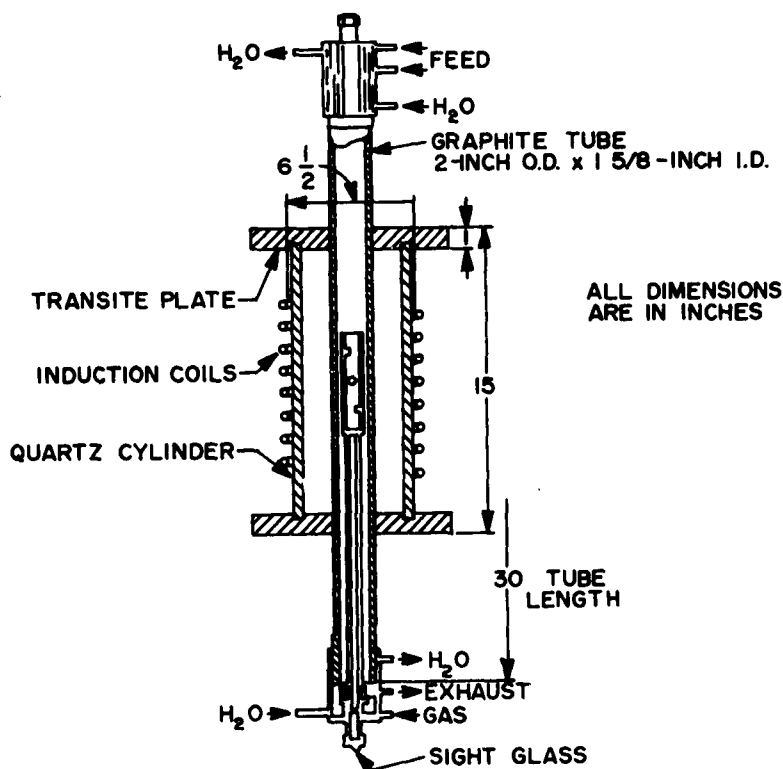


Figure 11. Graphite Tube Furnace Constructed by Merz

Pyrolytic decomposition of silanes and of silicon tetrachloride and hydrocarbons, in a high-temperature vapor phase reaction for growth of β -SiC has been investigated by Armour Research Foundation.¹⁶ The system used is shown diagrammatically in Figure 12. For the introduction of controlled amounts of silicon and carbon into the reaction chamber, the following requirements must be fulfilled:

The carrier gas must be thoroughly purified.

The flow of carrier gas through the dispersion bottles must be accurately controlled.

A moderately wide operating range is required.

The temperature of the volatile silicon and carbon containing components must be controlled.

The vapors in the saturated carrier gas must be mixed effectively.

The carrier gas, argon at a pressure of 5 psi in this case, was purified by passing over a titanium sponge at 700°C and then into a cold trap to remove any condensable vapors. The pure carrier gas is then split into three streams passing through meter valves. One of these streams is used for the volatile carbon compound, one is used for the volatile silicon compound, and one acts as a diluent. The reactants used were silicon tetrachloride and toluene. Since the SiCl_4 is more volatile than toluene, it is kept in an ice bath, whereas the toluene is immersed in a bath whose temperature is maintained at a value calculated to give the desired gas phase compositions. After the separate argon streams have been saturated with SiCl_4 and toluene, they move into the cylindrical vortex chamber where they meet the diluent stream and are mixed thoroughly before entering the furnace. The ratio of SiCl_4 to toluene in the gas phase, the total concentration of the reactants, and

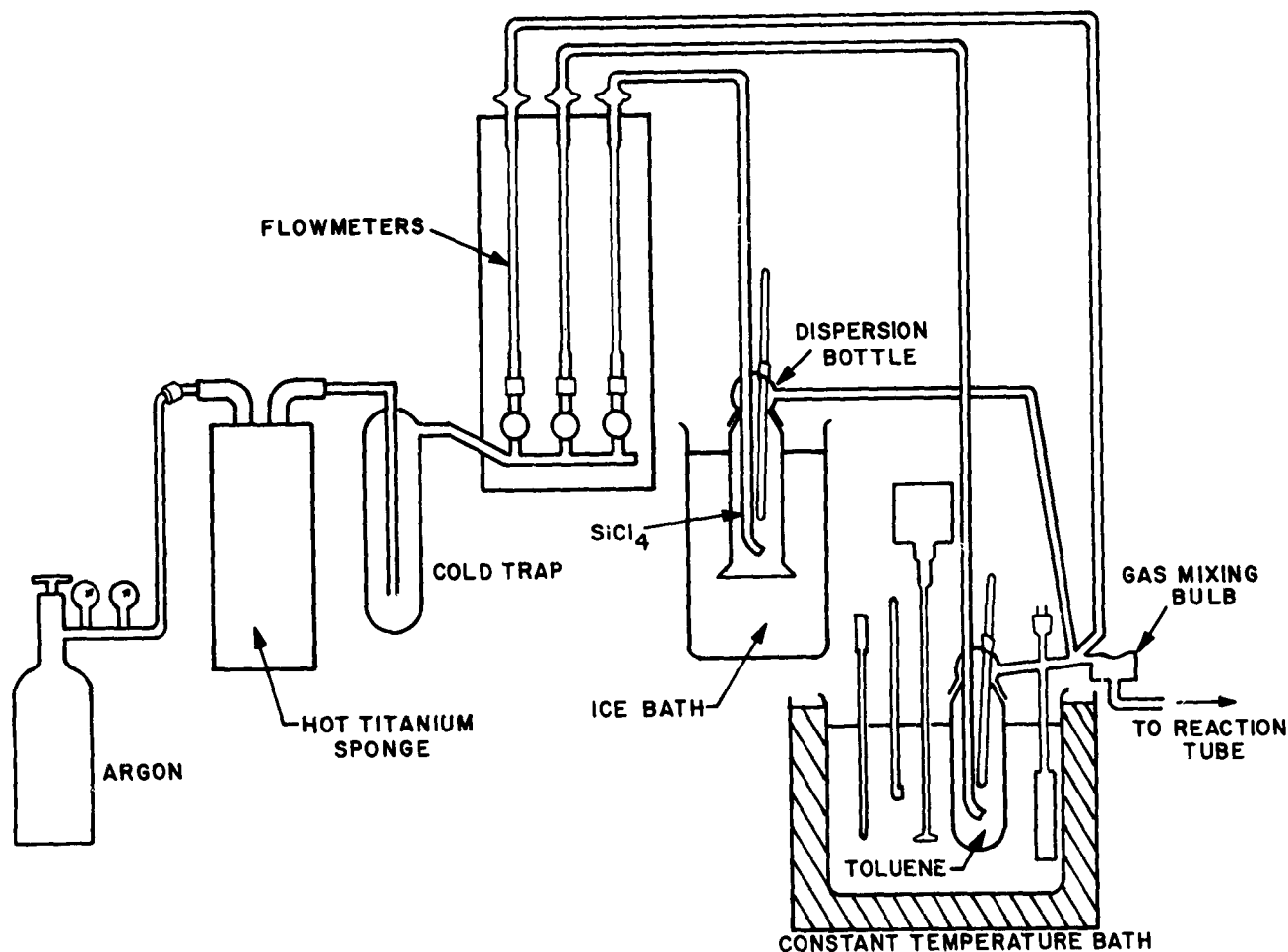


Figure 12. Vapor Phase Train

the transit time through the reaction tube are controlled by varying the temperature in the water bath, the flow rates through the dispersion bottles, and the flow rate of the diluent stream.

The furnace, which would operate at temperatures ranging from 1500° to 2200°C, was constructed from graphite furnished by the National Carbon Company. The power supply consisted of a motor-driven, 4-gang, Superior Electric Variable Autotransformer rated at 31.4 kilovolt amperes. The resistance element was fabricated from graphite. The shell and end plates were fabricated from $\frac{1}{4}$ -inch-thick stainless steel wrapped with $\frac{1}{2}$ -inch copper tubing. A graphite tube suspended between the inner flanges of the end plates forms the gas chamber. Thermax thermatomic carbon contains the heat radially while tantalum baffles protect the end plates from excessive radiation. Figure 13 is a schematic diagram of the furnace assembly. Introduction of the vapor phase components into the reaction tube and monitoring of the internal temperature are accomplished by means of the reaction tube assembly shown in Figure 14.

Using this apparatus, Armour Research Foundation was able to deposit large quantities of β -SiC. However, the growth rate for high-purity single crystals is quite small, about 0.1 millimeter per hour. The best crystals were light yellow in color and had dimensions of 1 to 2 millimeter length and 0.2 millimeter diameter. Trimethylchlorosilane proved to be the best of the various silanes used for satisfactory crystal growth.

Electrical measurements on pure and impure single crystals and of aggregates of β -SiC indicated an electron mobility of 32 centimeters per volt second, a thermal energy gap of 1.90 ± 0.10 electron volts, and a thermoelectric power of -105 volts per degree. Impure dark blue crystals were n-type with resistivity of 10^{-3} ohm-centimeter and 2×10^{19} impurities per cubic centimeter. Light yellow crystals had resistivities of 1 to 10 ohm-centimeter and 10^{17} to 10^{16} impurities per cubic centimeter.

Westinghouse Electric Corporation¹⁰ used thermal reduction of silicon compounds onto a heated substrate. The apparatus used for the vapor growth of SiC is shown diagrammatically in Figure 15. It consists of a gas saturation train and a vacuum-tight reaction chamber which encloses a resistance heater. The reaction chamber consists of a quartz bell jar and a silver-coated base plate through which the electrodes and gas inlet and exit tubes enter through vacuum-tight seals.¹⁷

The carrier gas, argon at a pressure of 5 psi in this case, was purified by passing over a titanium sponge at 700°C and then into a cold trap to remove any condensable vapors. The pure carrier gas is then split into three streams passing through meter valves. One of these streams is used for the volatile carbon compound, one is used for the volatile silicon compound, and one acts as a diluent. The reactants used were silicon tetrachloride and toluene. Since the SiCl_4 is more volatile than toluene, it is kept in an ice bath, whereas the toluene is immersed in a bath whose temperature is maintained at a value calculated to give the desired gas phase compositions. After the separate argon streams have been saturated with SiCl_4 and toluene, they move into the cylindrical vortex chamber where they meet the diluent stream and are mixed thoroughly before entering the furnace. The ratio of SiCl_4 to toluene in the gas phase, the total concentration of the reactants, and

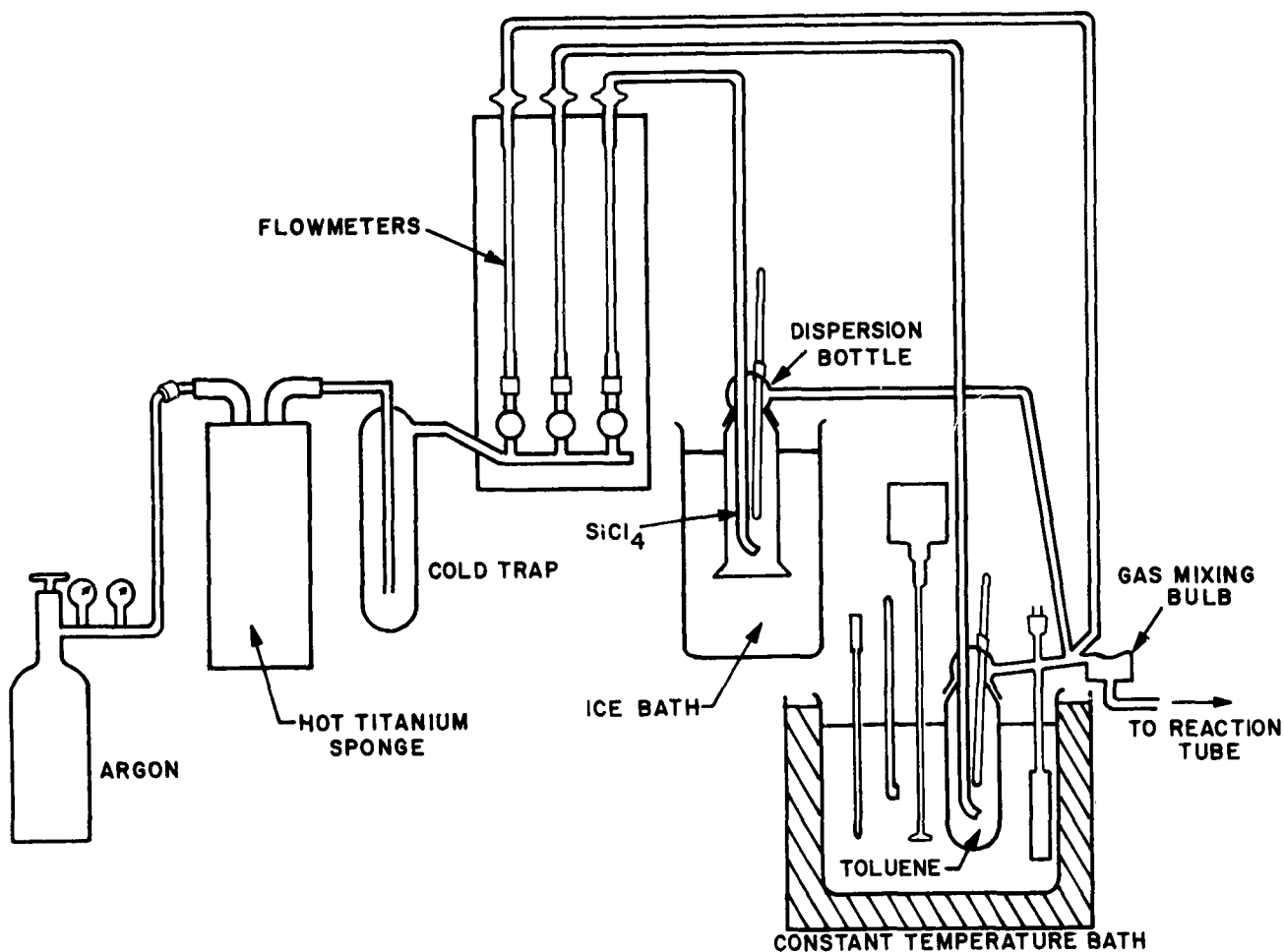


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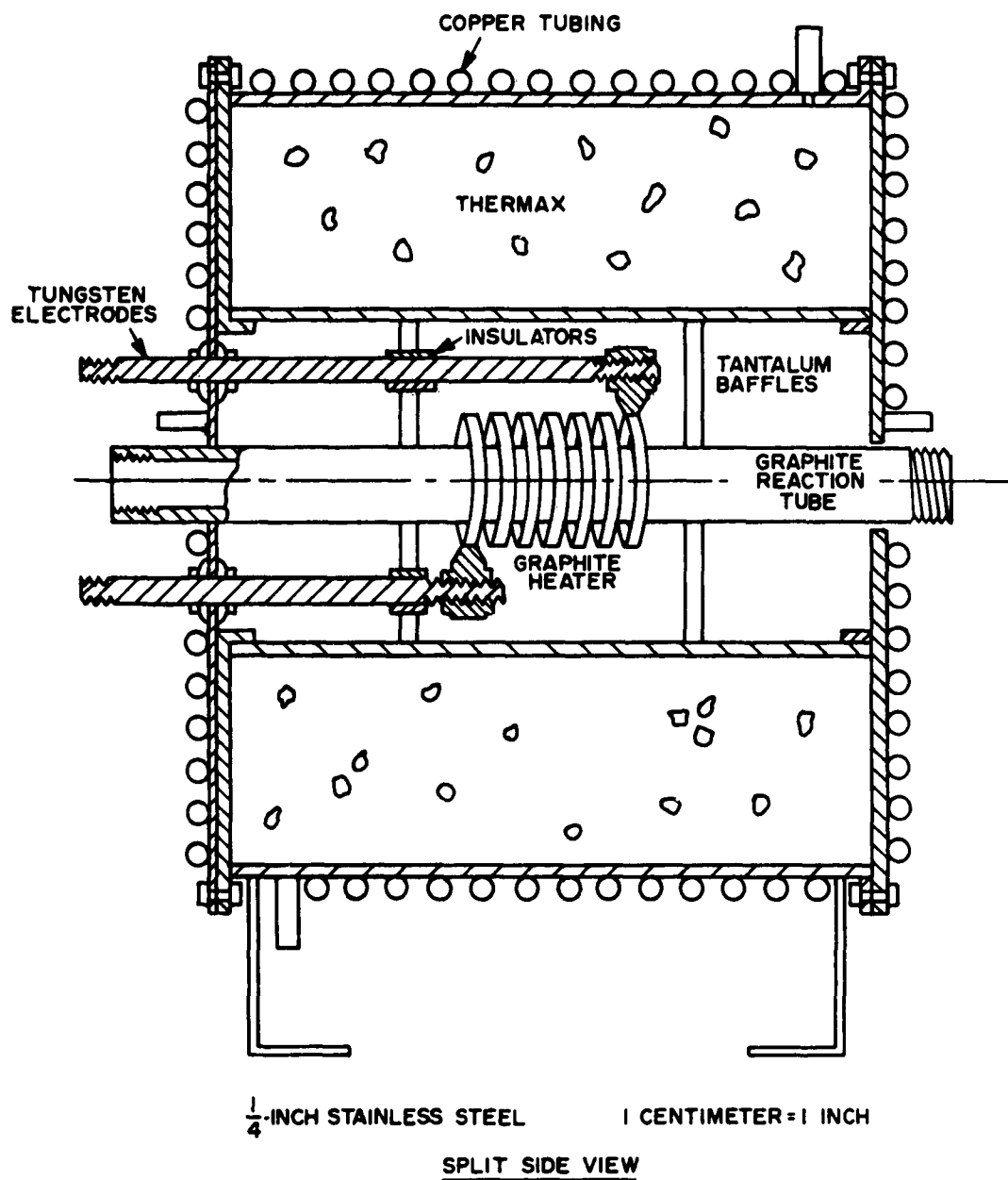


Figure 13. Furnace Assembly

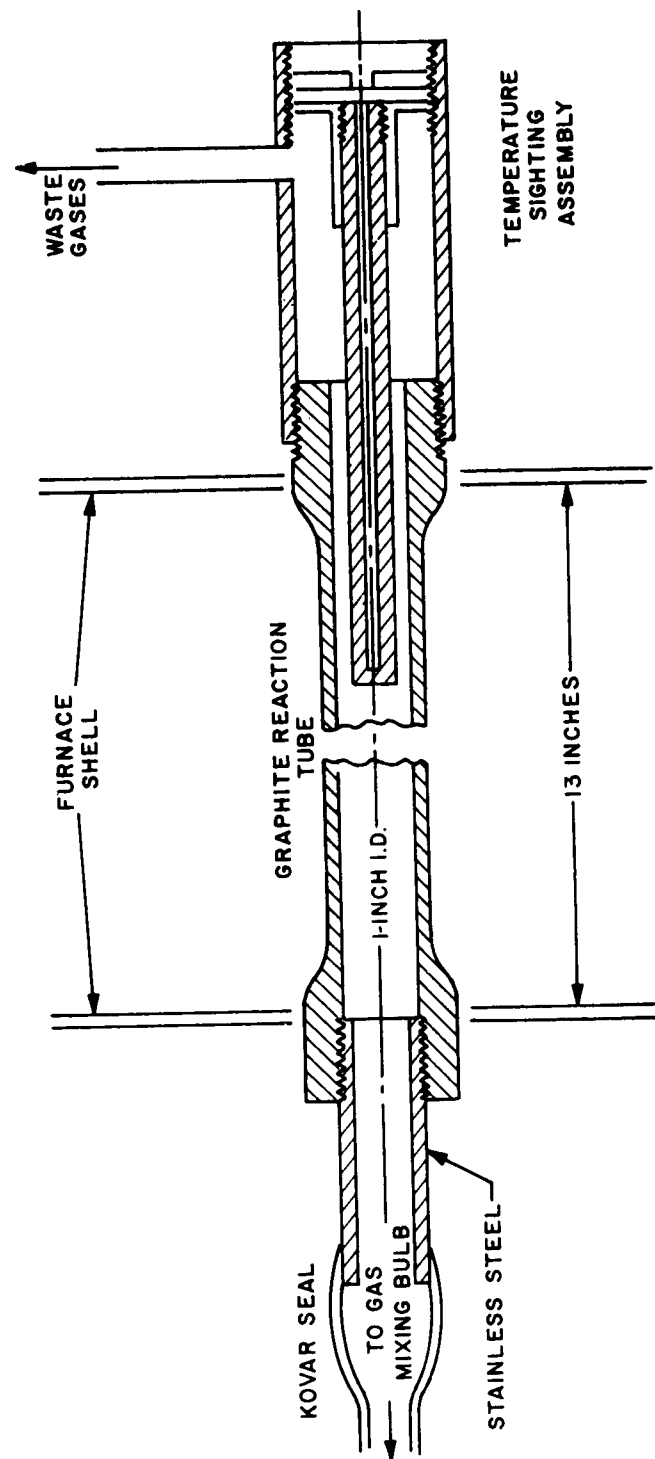


Figure 14. Reaction Tube Assembly

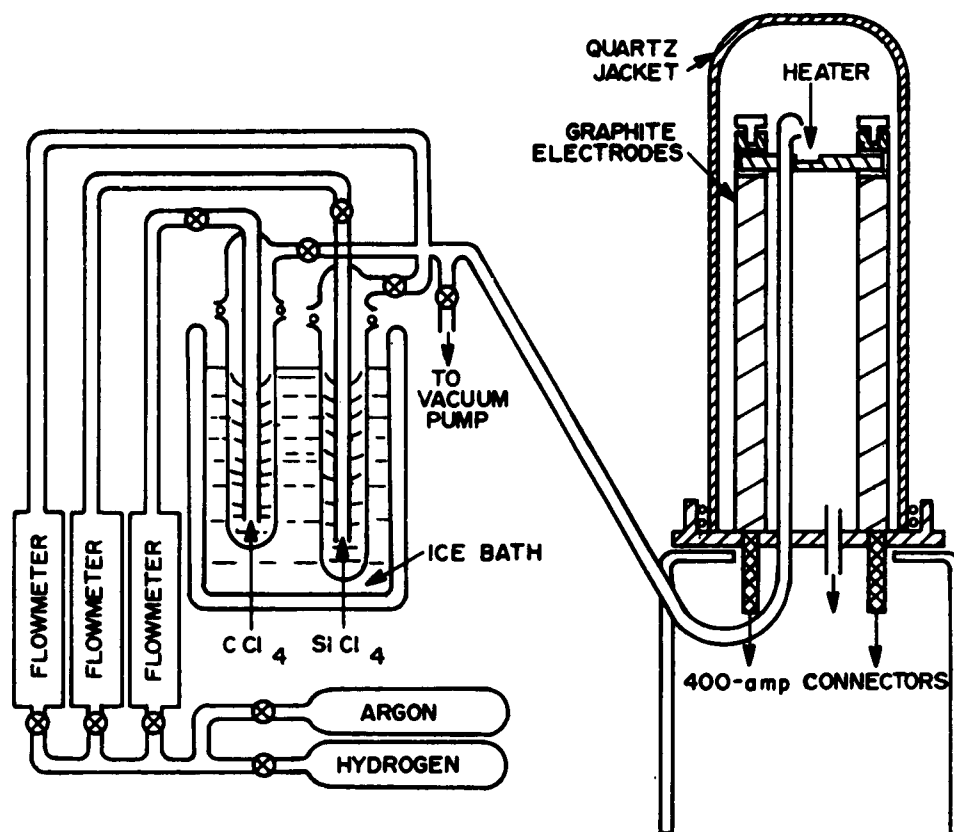


Figure 15. Vapor Growth Apparatus

Westinghouse conducted experiments to study the effects of reactant concentrations and crystal temperature on SiC epitaxial growth. The SiC platelet was heated on a flat graphite heater. In these experiments, the concentrations of SiCl_4 and CCl_4 were held at 0.4 percent and 0.2 percent, respectively, with a total hydrogen flow rate of 550 cubic centimeters per minute. Crystals are prepared for growth by first etching in a molten salt mixture of 2 grams of sodium peroxide and 6 grams of sodium hydroxide heated to 650°C for 2 minutes. The crystals are then washed in dilute hydrochloric acid and then placed in concentrated aqueous HF for 1 hour. Finally they are cleaned ultrasonically in methanol, covered with a Fisher lens paper and dried under an infrared lamp.

To study the effects of temperature on crystal growth, crystal temperatures of 1650° , 1700° , 1750° , 1800° , 1850° , and 1900°C , were used in separate experiments. At temperatures between 1650° and 1800°C , an epitaxial layer of cubic SiC was formed on the basal planes

of the hexagonal SiC substrate. However, none of the growth on the basal plane extended beyond the edge. In addition, clusters of tiny yellow cubic SiC crystals were usually nucleated at random on the surface of the crystal. The crystals that were heated to 1850°C and beyond were partially decomposed instead of exhibiting growth. Experiments using concentrations of 1.0 and 2.5 percent SiCl₄ with 0.5 and 1.3 percent CCl₄, respectively, gave essentially the same results. However, the number of yellow, cubic SiC crystallites was found to increase with an increase in the concentration of the reactants. In addition, the use of lower concentrations of SiCl₄ and CCl₄ appeared to give a layer containing fewer imperfections. Various modifications to the heater design failed to result in growth on the edge of a SiC seed by the hydrogen reduction of silicon and carbon halides.

An extension of the method used by Kendal was used by Raytheon,^{18, 19} consisting of the thermal decomposition of silicon and carbon-bearing gases on a heated substrate. Raytheon's apparatus is shown in Figure 16. The furnace consists of a water-cooled quartz tube in which a graphite tube is inductively heated. The gas to be decomposed is introduced into the reaction chamber through a water-cooled injector. Various gas compositions may be established by varying the temperature of the liquid starting materials through which the carrier gas is passed. Doping material, if desired, may be similarly introduced. The waste gases are trapped in a suitable train. Silicon tetrachloride and toluene were introduced by a hydrogen carrier gas into the hot zone at temperatures ranging from 1700° to 2200°C. Methane, carbon tetrachloride, or chloroform may be substituted for toluene without changing the experimental results. Trichlorosilane, SiHCl₃, has also been used in a few experiments to replace the silicon tetrachloride. This method resulted in crystals measuring 4 to 5 millimeters in diameter. The largest crystals are usually not single but consist of three or four single crystal areas.

5. Vapor-Phase Czochralski Method^{10, 11}

The Czochralski method of crystal growth has become a standard technique for growing single crystals from the melt. In this method, a single crystal is immersed into a supercooled melt and slowly withdrawn. The molten material solidifies on the seed crystal and large single crystals result. Westinghouse modified this technique in an effort to withdraw a single crystal from a supersaturated vapor of silicon carbide. The apparatus used for this study is shown in Figure 17. A stainless steel rod is attached to the pulling mechanism and enters the furnace through a double O-ring seal. A seed crystal is attached to a carbon rod which is threaded into the stainless steel rod.

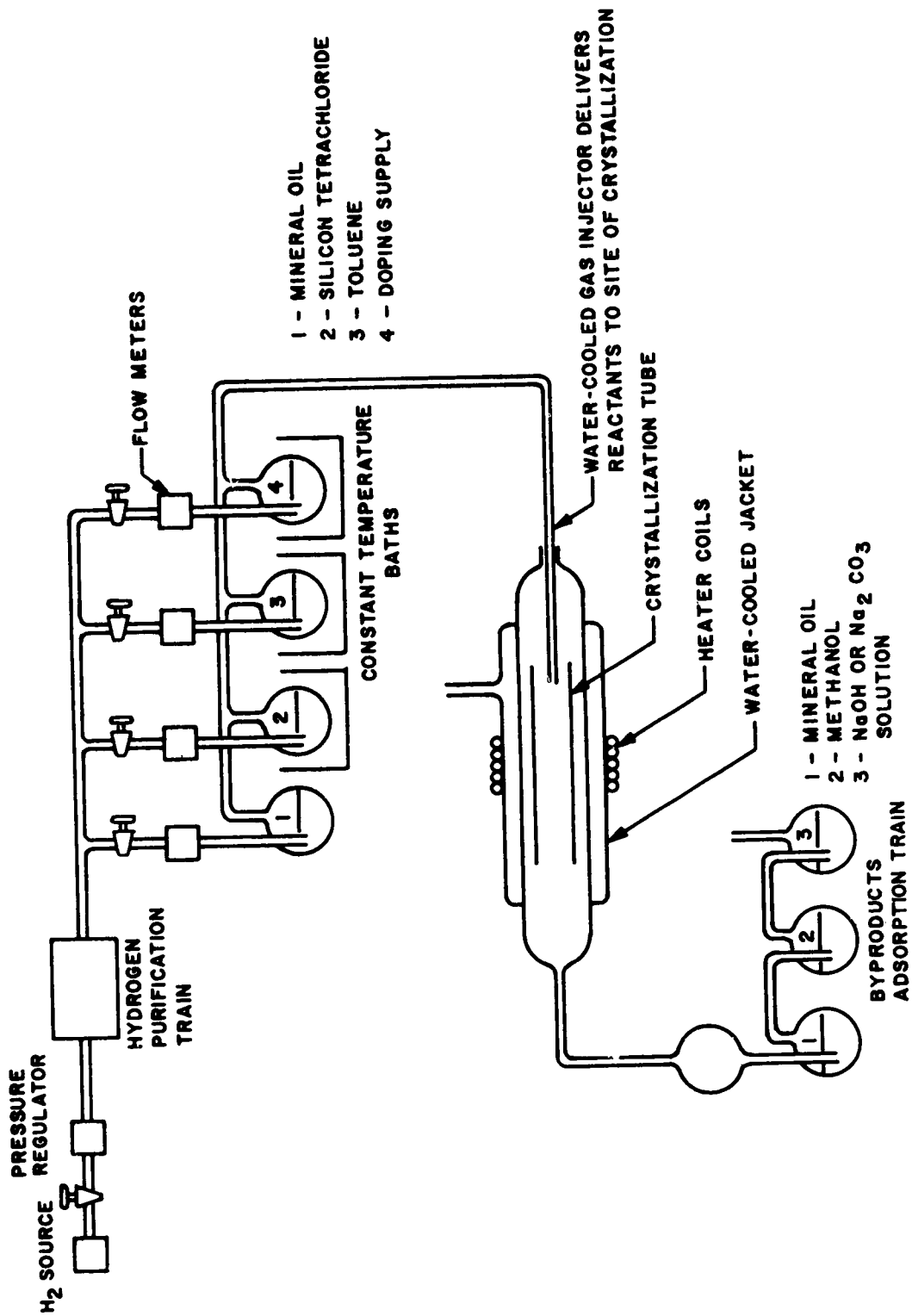


Figure 16. Schematic Diagram of Apparatus for the Preparation of Cubic Silicon Carbide Single Crystals

Pulling rates from 0.01 to 1.0 mil per hour were used. The initial results were negative in that the crystal decomposed. This effect was shown to be due to a lack of sufficient supersaturation of silicon and carbon in the center of the growth cavity, even though there was sufficient vapor near the cavity wall. The experimental arrangement was modified to permit greater control over the vapor supersaturation and ensure sufficient condensation of vapor on the seed in the center of the cavity. These modifications resulted in some growth on the basal plane. The growth appeared to be epitaxial with a high degree of surface perfection.

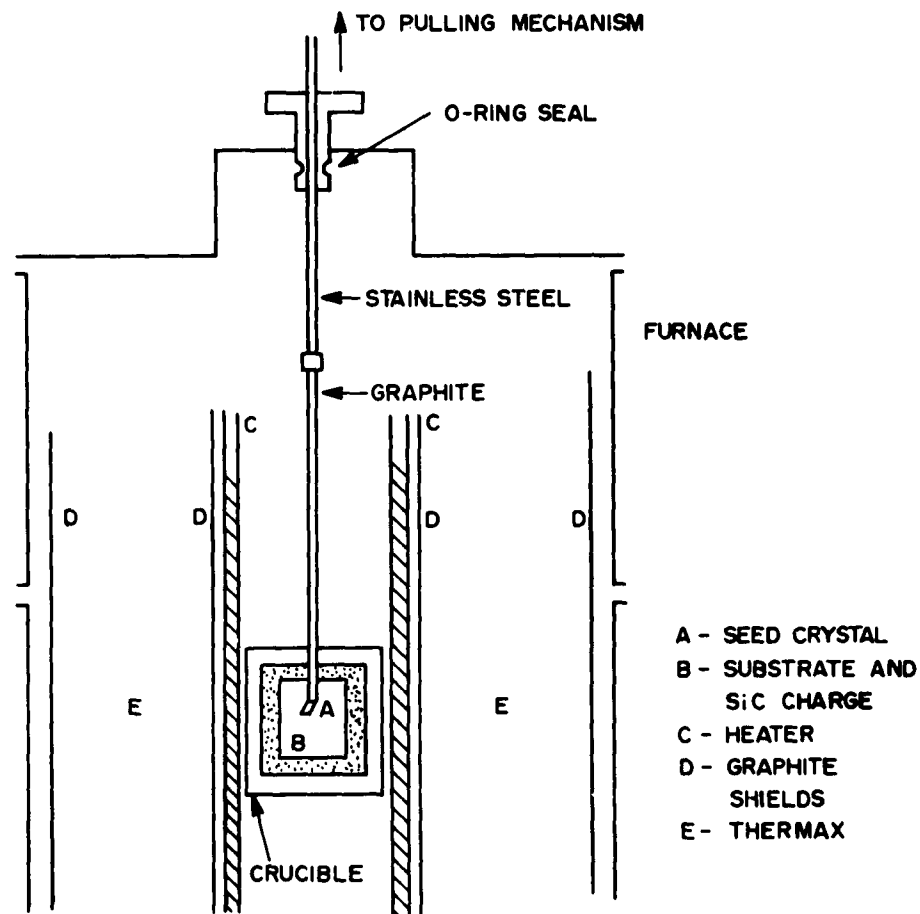


Figure 17. Vapor-Phase Czochralski Method

6. Epitaxial Growth

Hergenrother, et al,²⁰ of the Transitron Electronic Corporation, have shown that SiC can be grown from the vapor onto a seed crystal at low pressures, a method commonly known as epitaxial growth. For a seed crystal to grow from the vapor phase, it is necessary for molecules to be absorbed onto the crystal surface and then diffuse to surface steps. High supersaturation leads to spurious growth nuclei on the seed's surface, which destroys any chance of epitaxial growth. If, however, the supersaturation of the vapor is just enough to allow growth, but not high enough to allow nucleation, the seed crystal will grow by the addition of epitaxial layers.

The SiC seeds, employed by Transitron as a substrate to support epitaxial growth, were hexagonal in form with faces about $\frac{1}{2}$ -inch square. Their coloring depends on the type of impurities which are introduced into the lattice during crystal growth. A shiny black color indicates the presence of aluminum in the crystal which dopes the SiC so that it is electrically p-type; a transparent green color indicates that the impurity is nitrogen, resulting in n-type.

Transitron^{21, 22, 23} prepares the SiC by two methods. First, purified silicon is reacted with pure graphite. An analysis of the impurities in this material gave the following results:

| Element | Parts per Million |
|---------|-------------------|
| Fe | 1 |
| Ni | 5 |
| Al | 5 |
| V | 20 |
| Cu | 10 |
| Ti | 50 |
| Ca | 1 |
| Mg | 1 |
| B | 5 |
| Cr | 1 |

The second method consists of reacting highly purified silicon tetrachloride with toluene, producing another pure silicon carbide source material. Figure 18 shows the furnace used for epitaxial growth.² The crucible that holds the source charge of silicon carbide is heated by a carbon resistance heater. The heater is made from a vertically slotted carbon tube. The vertical slots increase the resistance of the heater. Two water-cooled electrodes, which are mounted on a water-cooled zirconium copper base plate, supply electric current to the

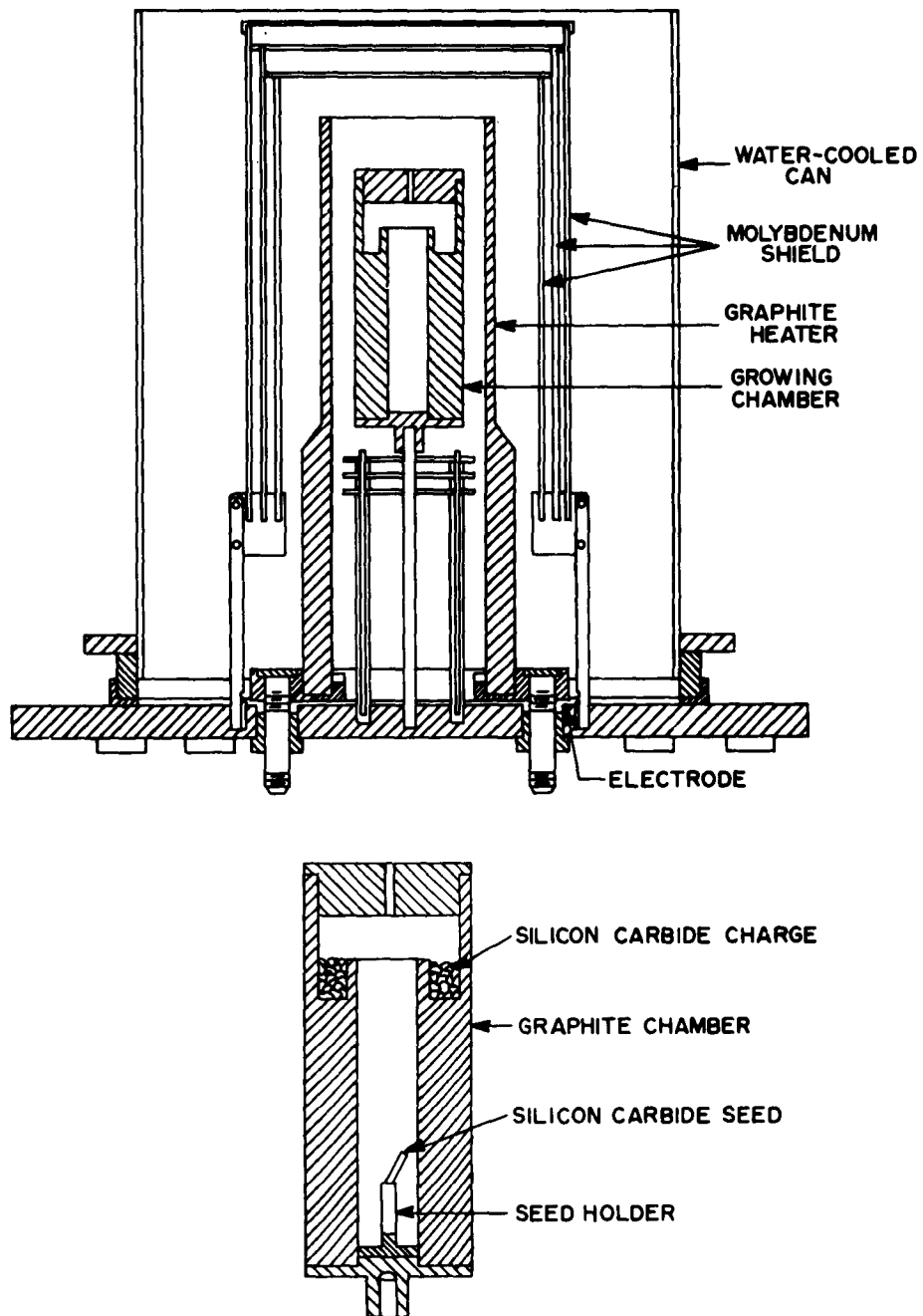


Figure 18. Vacuum Furnace and Seed Holder

graphite heater. The heater is surrounded by a cylindrical carbon shield and three concentric molybdenum cans for heat insulation. A carbon cover rests on the top of the carbon shield, and molybdenum discs cover the top of the shields to insulate the top of the crucible. Shields were used instead of carbon powder so that the furnace can be evacuated and purged to remove all unwanted gases. The electrodes and quartz viewing port are sealed with O-rings. Also, an L-gasket seals the junction between the can and the base plate so that the system can be pumped down to a pressure of 1 micron of mercury in about 10 minutes with a two-stage rotary vacuum pump. This system of heater and heat shields gives the furnace a low thermal inertia. It can be raised to the operating temperature in 3 to 5 minutes. Power leads, gas inlet, and vacuum pipes connected to the vacuum system pass through the base plate. The slotted graphite heater tube has an electrical resistance of about 0.33 ohm. In operation, the charge crucible is heated to about 2500°C while the seed is held at 2400°C. The distance between the seed and the charge is about 1 inch. Since the furnace design allows a swift temperature rise of the furnace parts, the seed achieves a temperature greater than 2000°C before enough silicon carbide diffuses from the charge crucible to cause random nucleation on the seed surface.

The graphite crucible is supported inside the heater by a graphite rod. Three molybdenum shields beneath the crucible cut down the free radiation to the base plate. Silicon carbide that is used for the source of vapors is located in an annulus at the bottom of the crucible chamber. The seed is suspended in a slot of the seed holder which stands on the bottom of the crucible. The top of the chamber is covered by a hollow graphite plug that provides a relatively tight gas seal. There is a hole through the bottom of the crucible for evacuation and backfilling. When a gaseous dope is introduced into the furnace, most of the dope penetrates through the crucible walls, since graphite is quite porous for gases at these temperatures.

Radiation transfers the major portion of heat at the temperature at which silicon carbide is grown. Therefore, the temperature of various parts of the crucible and of the seed is a function of their orientation to the heater and its open, unheated ends. With the charge near the center of the growing chamber, and with most of its surface area parallel to the heater, the charge is in the hottest portion of the chamber. Since the seed rests closer to the end of the chamber and it is oriented with most of its surface area facing vertically, it is cooler than the charge. The temperature is determined by orientation of the body with respect to the walls. The temperature of a seed, as a result, can be selected by proper orientation of the seed with respect to the slotted tube graphite

heating element. During epitaxial growth, helium is admitted to the growing chamber. The power supply for the slotted tube heater provides a maximum output power of 33 kilowatts. A single-phase saturable core reactor provides adequate control of the current to the heating element, and of the temperature of the crucible and seed.

There are three steps in the procedure for growing epitaxial layers of SiC:

Seeds must be cleaned and prepared.

The furnace must be loaded with the charge and seed before assembling the shields.

The furnace must be evacuated, outgassed, and brought to temperature after the water-cooled steel can is fixed into place over the entire furnace assembly.

Seed preparation is the first step in the procedure for growing epitaxial layers. These crystals are mounted on a steel plate with a hard wax, and the bulk of material is ground off with a diamond or a silicon carbide grinding wheel to a thickness of 0.035 inches. The ground face is parallel to the flat (0001) face on the original crystal. Before being etched, the platelets are polished with a 1-micron particle-size diamond polish. Then the seed platelets are removed from the steel plates, cleansed of wax, and etched for $\frac{1}{2}$ minute in a mixture of 50 percent potassium nitrate and 50 percent potassium hydroxide at 500°C. This molten mixture removes any surface impurities, such as the oxides of silicon, by removing about 0.001 inch of silicon carbide from the seed surface. These seeds are then washed several times in hot deionized water and isopropyl alcohol, to remove all traces of the etching chemicals. After this the seeds have a polished glass-like appearance on the side which was the original (0001) face; it is shiny but not quite as smooth as the ground face.

For growing n-type epitaxial layers onto p-type seeds, the following procedure is used: First, a seed of bluish-black silicon carbide (aluminum doped), with a flat (0001) face is prepared. This seed is fitted into a slot that is cut in the carbon seed holder shown in Figure 18. Next, a charge of about 10 grams of aluminum-doped carbide grain is loaded in the crucible. The assembled crucible is placed in the center of the heater on a graphite rod. Once shields are put into place, the water-cooled can is lowered and the system is evacuated. Then the furnace chamber is filled with purified helium to a pressure of 20 inches mercury while maintaining a flow of 0.3 liter of helium per minute.

At this point, a current of 280 amperes is turned on at 85 volts for 1 hour. The furnace heats up to operating temperature within a few minutes after the current is turned on, and the epitaxial film starts to grow. Nitrogen is admitted into the system at a rate of $\frac{1}{2}$ cubic centimeter per minute, after 20 minutes of epitaxial growth. After an additional 20 minutes, the nitrogen flow is raised to 3 cubic centimeters per minute and held there for the remaining 20 minutes of the run. Consequently, the remainder of the layer that is built up epitaxially will be heavily doped n-type to aid the eventual connection of ohmic contacts.

Westinghouse Electric Corporation,²⁴ under contract AF(604)-8499, investigated epitaxial growth of cubic SiC on a hexagonal SiC substrate. The apparatus used for these experiments is shown diagrammatically in Figure 19. The reactor is a water-cooled quartz tube held vertically. Inside is a graphite block susceptor mounted in a quartz holder. The SiC substrate is placed on top of the graphite block, and suitable provisions are made for admitting the reactant gases.

In these experiments, a SiC crystal was divided into two pieces and cleaned in hydrofluoric acid followed by a methanol rinse. The two pieces were then placed on the graphite heater so that the faces to be grown on were on opposite orientation, i. e., one was the silicon face and the other was the carbon face. There was a marked difference between the growth obtained on these two faces. This result may be compared to the difference observed on etching these two faces. The latter difference is believed to be due to the slight ionic character of the silicon-carbon bond, which, because of the orientation of silicon-carbon dipoles in layers, makes the silicon face positively charged with respect to the carbon face. The growth obtained on the carbon face was similar in appearance to that observed in the growth of a silicon layer onto an oxide-coated silicon surface. In the latter growth, the presence of oxide interferes with the formation of silicon-to-silicon bonds.

An increased ratio of silicon tetrachloride to carbon tetrachloride from 1 to 1 (the usual ratio) to 4 to 1 showed no marked effect on the mosaic pattern of a cubic layer. There was also no significant change in the growth rate. This indicates that the SiCl_4 concentration in the reactor is not a rate determining factor. Since graphite is present in the reactor, H_2 transport will ensure an excess of carbon. Therefore, it is probable that the rate-determining parameter at constant temperature is diffusion across the boundary layer between the growing surface and the vapor phase.

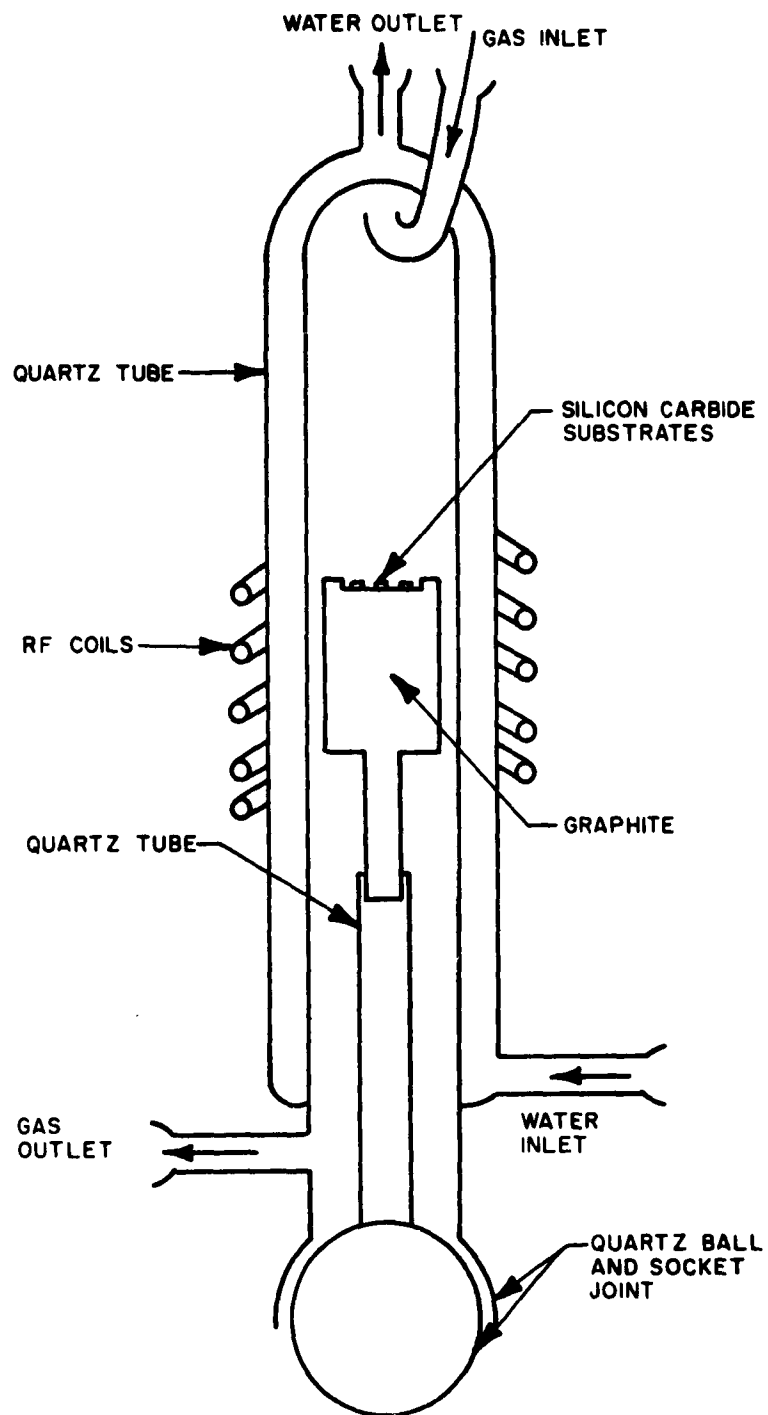


Figure 19. Epitaxial Growth Reactor

The cubic growth obtained by using fast growth rates at substrate temperatures of 1700°C gave valuable information. When the growth time was reduced to about 1 minute, the nuclei were seen to be forming in concentric circles. These are probably the edges of spiral growth steps on the surface of the substrate.

There are two current theories applicable to the growth of crystals from the vapor phase. One depends upon the formation of a two-dimensional nucleus for the growth of a new crystalline layer, and the other postulates growth with screw dislocation. The dislocation presents a self-perpetuating step at which growth takes place. Growth by screw dislocation is possible with much lower supersaturations than those required for the formation of a two-dimensional nucleus.

7. Growth from Solution

The expectation that pure SiC crystals might be grown from liquid silicon solutions is based on the fact that SiC bonds are considerably stronger than the average silicon-silicon and carbon-carbon bonds. An ideal solvent for growing SiC crystals would readily dissolve SiC and have considerable temperature dependence on the solubility. Moreover, the dissolution process would be reversible. In fact, Stanford Research Institute lists the following desired solvent characteristics for growth from supersaturated solutions:²⁵

The solvent should dissolve the crystal components to an appreciable extent.

The solubility of the crystal components should depend considerably on temperature.

A continuous transfer of supersaturated solution to the growing crystal surface is necessary.

The solvent should not form compounds or solid solutions with the crystal at growth temperatures.

If possible, the solvent should have an ion in common with the solute, or, if not, one in which the ionic radii differ as much as possible from those of the solute.

The viscosity of the solvent should be low.

The solvent should be such that if it is present as an impurity in the crystal, it will not influence the useful properties of the crystal.

The vapor pressure of the solvent should be low so that the desired compositions can be easily maintained.

The melting point of the solvent should be much lower than that of the solute.

The solvent should be soluble in some medium in which the synthesized crystal is insoluble.

Based on the above conditions, molten silicon was selected by Stanford Research Institute as the solvent with alloying elements added either to dope the growing crystals or to modify the solubility of carbon in silicon. Figure 20 is a plot of carbon solubility data, indicating that the first two requirements above are adequately fulfilled in the temperature range of 1500° to 1700°C. Figure 21 gives the approximate solubility data for carbon in a 70 iron - 30 silicon alloy. It appears that the carbon solubility in this alloy is 8 to 10 times that in pure silicon in the same temperature range, but the dependence of solubility on temperature is somewhat less. The general approach used by Stanford Research Institute consisted of saturating molten silicon or molten silicon-metal alloy with carbon from a silicon-carbide-coated graphite crucible, and then by maintaining a suitable thermal gradient, a super-saturated region in the melt is produced from which SiC recrystallizes. Single crystals of β -SiC were produced by this method, the largest of which were in the form of triangular plates 3 to 5 millimeters on a side and 10 to 30 microns thick. The best crystals were obtained by permitting growth to occur within the body of the silicon melt. The crucible was held at an average temperature of 1540°C, with a vertical thermal gradient of 30°C per inch, with the cooler portion being at the bottom, for 24 hours. It was then cooled at the rate of 18°C per hour.

The crystal-growing furnace employed by Stanford Research Institute was a modified Czochralski type. The power supply was a 50-kilowatt saturable-core reactor feeding through a stepdown transformer to a graphite resistance unit. The water-cooled shell was insulated from the hot zone by three concentric molybdenum cylinders. The crucible was mounted on a graphite cylindrical spacer which supported three molybdenum heat shields forming the base of the hot zone. The spacer was, in turn, mounted on a water-cooled crucible support tube which could be rotated and traversed vertically through the hot zone. The furnace lid had a central port for admission of a seed rod or hot probe. The seed rod could be rotated and traversed through the hot zone either at high speed or at controlled rates varying from 80 microns per second to less than 1 micron per second. Inert gas was admitted to the furnace through an all-copper system containing a liquid nitrogen cold trap filled with Linde molecular sieve. The entire unit could be evacuated to less than 10^{-6} millimeter by means of a trapped oil-diffusion pump.

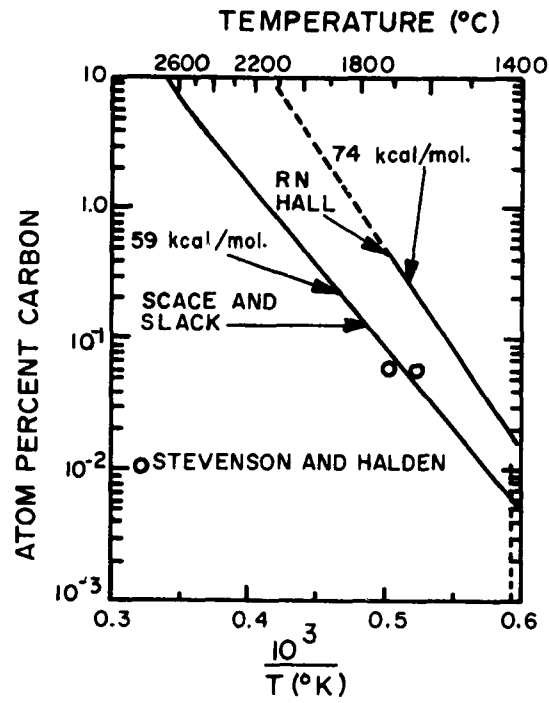


Figure 20. Solubility of Carbon in Liquid Silicon

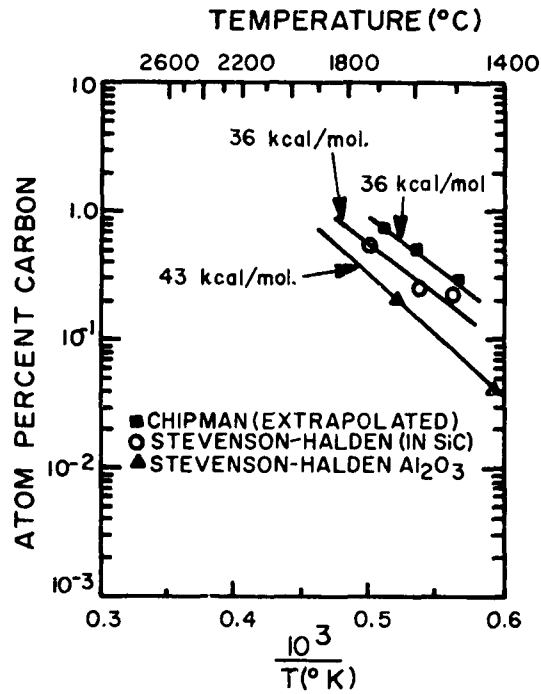


Figure 21. Solubility of Carbon in a 70-Fe, 30-Si Alloy²

Temperature control was obtained by means of a Rayotube, sighting through a quartz window in the base of the crucible support tube on the base of the crucible. The putput signal was bucked against a standard potentiometer, and the resultant signal was fed into a microvolt amplifier prior to reaching a Speedomax H recorder-controller. By this means, thermal cycling was held within $\pm 0.1^\circ\text{C}$ during normal operation. The unit was programmed to provide linear heat-up and cool-down control.

The normal operating procedure was to position the crucible in the uniform-temperature zone, to evacuate the furnace to 10^{-6} millimeter, and then to heat it slowly to 1200°C . At 1200°C , purified helium was admitted (under 2 pounds positive pressure) and a slow gas flow rate was set by observing the gas discharge through a diffusion-pump-oil standpipe. The furnace was then heated to the operating temperature. After allowing a period of 30 to 60 minutes for temperature equilibrium, the crucible was moved slowly into the gradient region of the hot zone, maintaining the coolest portion of the crucible at constant temperature.

Studies with various temperatures, temperature gradients, and pull rates revealed that the best crystals were obtained by permitting growth to occur within the body of the silicon melt. Stirring of the melt by opposite rotation of the crucible and seed was found to be essential for a reasonable growth rate.

In nearly all of these studies, four general types of crystals were found: (1) whiskers (one-dimensional growth), (2) plates (two-dimensional growth), (3) polyhedrons (three-dimensional growth), and (4) dendrites and twinned crystals. The last of these types predominated under all conditions except when slow growth rates and short growth times were employed. At 0° temperature gradient, no crystal growth occurred at growth times up to 48 hours. With gradients of 1° to 5°C per inch, whisker growth predominated, and small crystal yields were obtained even after long growth times. These whiskers were 3 to 7 millimeters in length and 10 to 20 microns in cross section. They were uniform in appearance and flexible, with tensile strengths exceeding 350,000 psi - the limiting strength of the epoxy mounting adhesive used in these measurements.

Gradients in the range of 5° to 25°C per inch resulted in the appearance of some plates. It is under this condition that nearly all of the crystal plates suitable for electrical measurements were grown. These plates were normally in the form of thin (10 to 30 microns) triangles or laths with (111) faces.

At higher thermal gradients, the growth of dendrites and twinned crystals resulted in large quantities of completely intergrown material and in almost no single crystals.

A technique which permitted maintenance of supersaturation through the body of the melt, by cooling the solution slowly, produced the best crystals. The best combination of conditions was found to be an average temperature of 1500°C, a run time of 24 hours, and a cooling rate of 18°C per hour. A normal yield per run was 10 to 20 triangles and trapezoids 1 to 2 millimeters on a side, several laths up to 7 millimeters long and 0.5 to 1 millimeter across, and 1 or 2 plates 3 to 5 millimeters on a side.²⁵

Raytheon Company also investigated the growth of β -SiC under contract AF 19(604)6133.^{18, 19} Figure 22 shows a schematic diagram of the furnace used. The silicon is placed in a totally-enclosed graphite crucible located at the center of a graphite sleeve which can be heated by the longitudinal passage of current. Radiation shields are located above and below the graphite crucible so as to produce a temperature gradient which varies from the hot center of the crucible to a slightly cooler bottom. To prevent evaporation of silicon, a pressure of argon gas is maintained in the furnace. The argon is regulated by a valve and is purified (by passing it through a titanium-chip reactor held at 800°C in a stainless steel container) before it enters the furnace.

The temperature gradient is of considerable importance in determining the size of the crystals. Different combinations of graphite radiation shields above and below the reaction crucible were investigated. The combination resulting in the most successful growth had three graphite shields above and four below the crucible. This caused the temperature gradient along the crucible to be approximately 35°C, the bottom being cooler. The best crystals were obtained at 1570°C and 400 psi for 15 hours. The size of these crystals ranged from 0.050 inch after 15 hours to 0.100 inch after 60 hours.

8. Growth by the Travelling Solvent Method

Tyco Laboratories, Incorporated, studied the growth of SiC by the travelling solvent method under contract AF 19(604)-8803.²⁶ A suitable solvent for this method of growing crystals should dissolve the compound to be grown, have low solubility in the compound, and have a melting point much lower than that of the compound. Tyco Laboratories examined the use of chromium, platinum, and silicon as solvents.

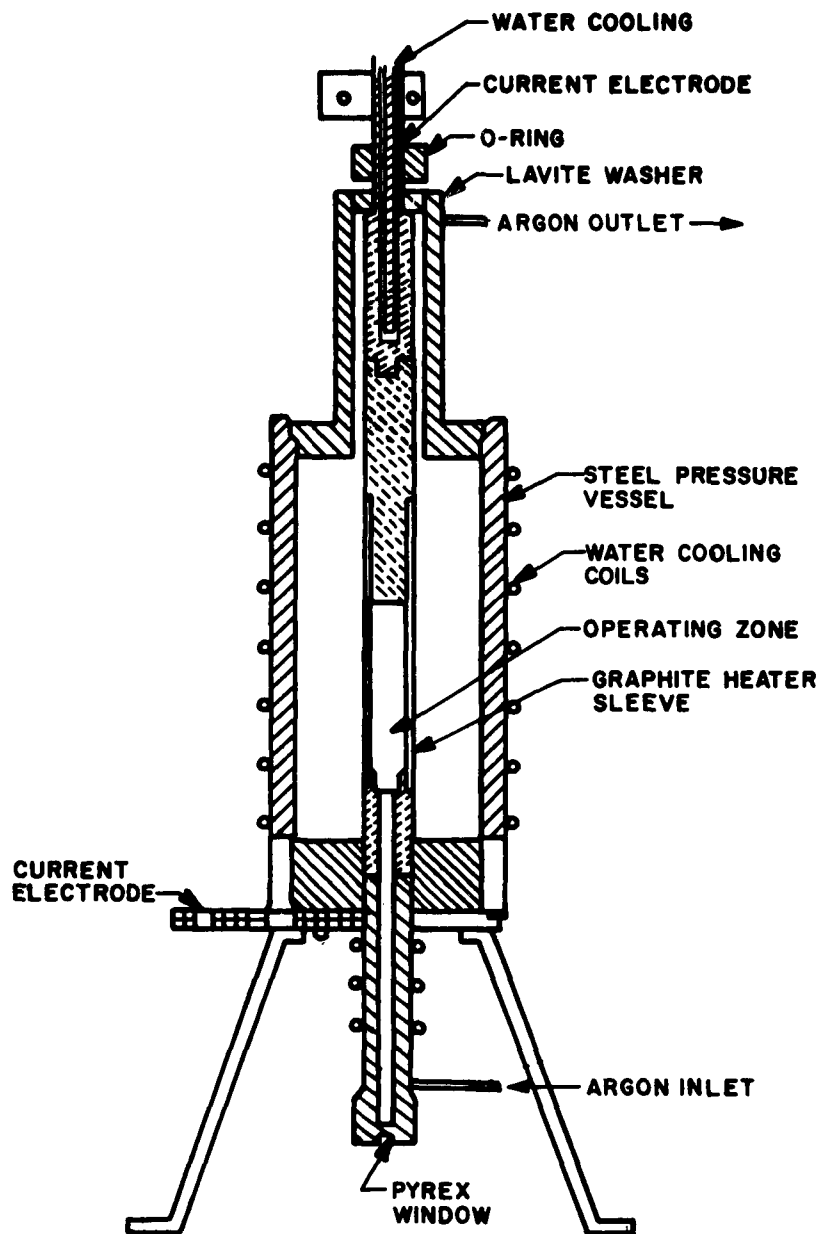


Figure 22. Longitudinal Section of the Graphite Pressure Furnace for Growing SiC Crystals

In the application of this method, a temperature gradient is impressed across a thin solvent zone sandwiched between two pieces of the solid to be grown. However, since the equilibrium solubility is greater at the hotter interface, a concentration gradient is established and solute diffuses across the liquid zone and precipitates onto the cooler seed crystal. The driving force for passage of the solvent zone is provided solely by the concentration gradient which is a function of both the temperature gradient and also the slope of the liquidus at the particular temperature of growth.²⁷

Zone passing experiments in the Pt/SiC and Si/SiC systems proved that the zone movement in these systems was too small for growth of crystals of practical value. However, Travelling Solvent Method has been successfully used for the growth of SiC from chromium and chromium alloy solvents. Relatively large SiC single crystals (up to $\frac{3}{8}$ inch long in the C direction and about $\frac{1}{4}$ inch square) were grown by the successive passage of six molten zones.

Initial efforts of crystal growth were hindered by difficulties encountered in the wetting of SiC surfaces with chromium. Good wetting was achieved when the SiC surfaces were cleaned by the following procedure: After the specimens were machined to a suitable size and shape, they were heated by electron bombardment to about 1300°C in a vacuum of 10^{-9} to 10^{-10} millimeter of mercury. A thin film of chromium was then evaporated from a heated tungsten filament onto the specimens. The apparatus used for specimen preparation is shown schematically in Figure 23.²⁶

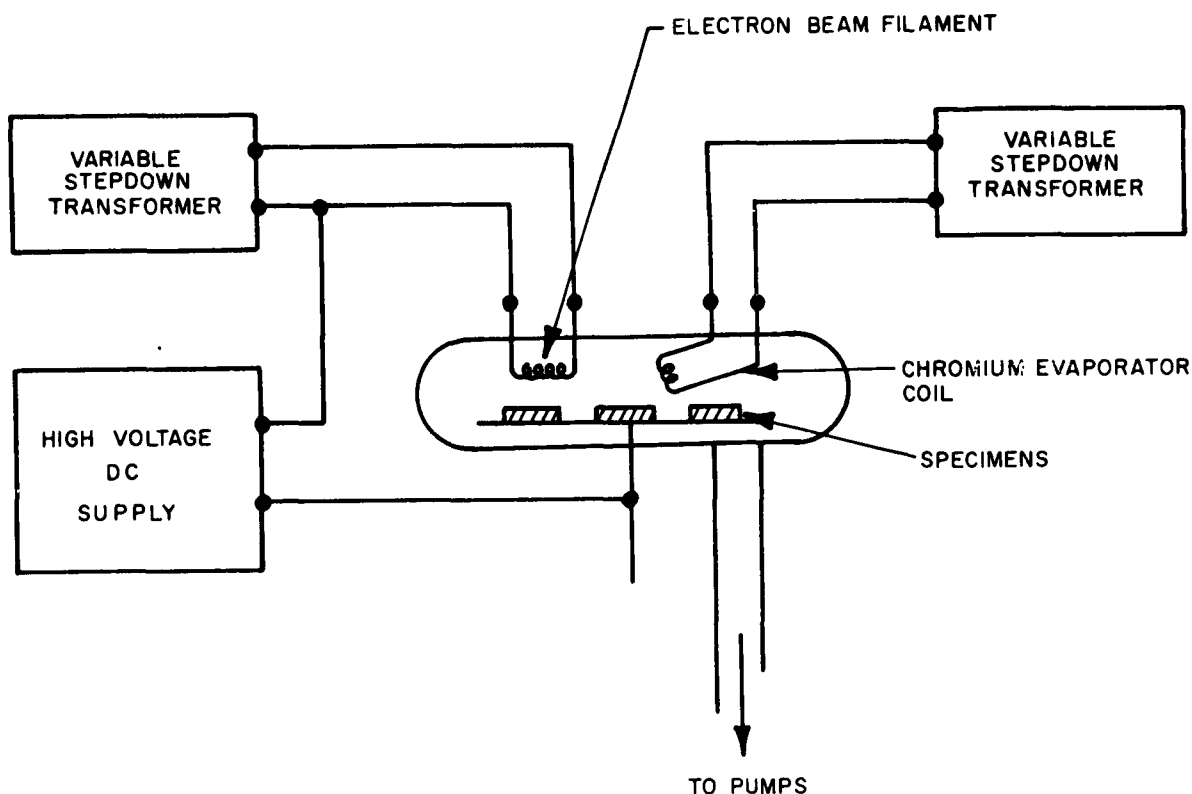


Figure 23. Schematic of Vacuum System with Electron Beam Heating and Chromium Evaporation Facilities

Section III. PROPERTIES OF SILICON CARBIDE

Considerable variations in the electrical, optical, and physical properties of SiC single crystals have been reported in the literature. Many of these differences arise from extreme difficulties in preparing pure SiC single crystals. Unfortunately, purities and complete sample descriptions are seldom presented by investigators. In addition, the stability of SiC limits the accuracy of analytical techniques that can be used for measuring impurity concentrations. Electrical studies are normally limited by the lack of suitable single crystals and the difficulty in attaching reliable contacts to the SiC surface. Stanford Research Institute studied SiC rather extensively under contract NObsr-72772. The final report under this contract²⁵ contains a literature survey which summarizes quite adequately the properties of SiC. Many of these properties will be reproduced here. Where newer data are available, they will be summarized by the agency or company which conducted these measurements.

Some typical published results of emission spectrographic analyses of several types of SiC are shown in Table I.

Table I. Typical Emission Spectrographic Analyses of Silicon Carbide

| Impurity | Black α -SiC | Green α -SiC | | | Colorless α -SiC | | β -SiC |
|----------|---------------------|---------------------|-----|-------------|-------------------------|-----|--------------|
| | ppm | ppm | ppm | ppm | ppm | ppm | ppm |
| Fe | 10 | 10 | <10 | 36 - 417 | 1 | 10 | 300 |
| Al | 10,000 | 60-100 | 370 | | 16 | 10 | 10 |
| V | 15 | 10 | 18 | | 25 | | 10 |
| Ti | >22 | 50 | 23 | | 15 | | 20 |
| Cu | | 0.5-30 | | <0.05 - 0.3 | | tr | 1 |
| Ca | | 5 | | | | | 10 |
| Mg | | 2-50 | | | | | 2 |
| Mn | | 0-15 | | 0.1 - 0.4 | | tr | |
| Ni | 3 | | 3 | 3-5 | 1 | | |
| B | 10 | | 0 | | 0 | | |
| Mo | | | | <0.5-2 | | | |
| Ag | | 0-10 | | | | | |
| Co | | | | | | | |
| Zn | | | | 0-0.16 | | | |

1. Band Gap

α -SiC

| <u>Value</u> | <u>Investigator</u> | <u>Remarks</u> |
|---|--|--|
| 3 electron volts | Weigel ²⁸ | |
| 3.32 - 6 x 10 ⁻⁴ T electron volts | Lely and Kroger ²⁹ | in the temperature range 470° to 1000°K |
| 2.86 electron volts | Choyke and Patrick ³⁰ | at 300°K |
| 2.9 electron volts | Philipp ³¹ | at 300°K |
| 2.83 electron volts | Patrick ³² | at 300°K on black, p-type crystal |
| 2.34 - 5.6 x 10 ⁻⁴ T electron volts | Constable and Feridan ³³ | temperature range 1140° to 1425°C |
| 3.1 electron volts | Racette ³⁴ | at 0°K on n-type single crystal |

β -SiC

| | | |
|------------------------|--------------------|---|
| 2.8 electron volts | Lely and Kroger | |
| 2.62 electron volts | Philipp | at 300°K |
| 1.90 electron volts | Pohl ³⁵ | microcrystalline aggregates up to 1300°C |

2. Electron Mobility

α -SiC

| | | |
|---|-------------------------------|--|
| 100-140 centi- meter ² per volt second | Lely and Kroger ³⁶ | |
| 100 centimeter ² per volt second | Hall ³⁷ | at room temperature in n-type α -SiC crystals with resistivities of 0.1 to 1 ohm-centimeter |

The mobility was found to decrease with increasing temperature according to the expression

$$\mu_H = aT^{-b}$$

where $b = 1.5$ to 1.8 .

3. Hole Mobility

α -SiC

| <u>Value</u> | <u>Investigator</u> | <u>Remarks</u> |
|---|---------------------|---|
| 10-25 centimeter ² per volt second | Lely and Kroger | at room temperature. The value decreases with increasing temperature according to $\mu_H = aT^{-b}$ where $b = 2.2$ to 3.0 . At low temperatures the hole mobility decreases with decreasing temperature. |

β -SiC

| | | |
|--|-------------------------|--|
| 32 centimeter ² per volt second | Pohl | on green β -SiC crystal having a resistivity of approximately 1.85×10^{-3} ohm-centimeter. |
| 70 centimeter ² per volt second | Warshauer ³⁸ | at 25°C, and 20 centimeter ² per volt second at 1100°C for n-type solution-grown β -SiC with carrier concentrations in the range 10^{19} to 10^{20} and resistivities of 10^{-2} to 10^{-3} ohm-centimeter. |

Some typical measurements of the electrical conductivity of SiC are shown in Figure 24. Values for the electrical conductivity cover a range of approximately 10 orders of magnitude, depending on purity.

A summary of electrical properties which have been estimated or calculated for α -SiC at room temperature and at 650°C is given in Table II. Few data of this type are available for β -SiC.

The data on the properties of SiC crystals just presented represents a summary of Stanford Research Institute's survey which covers the literature published prior to 1961. No attempt was made to verify any of these data. In many instances, there are no newer data found in the literature; however, where more recent data were available, they will be summarized in the following pages.

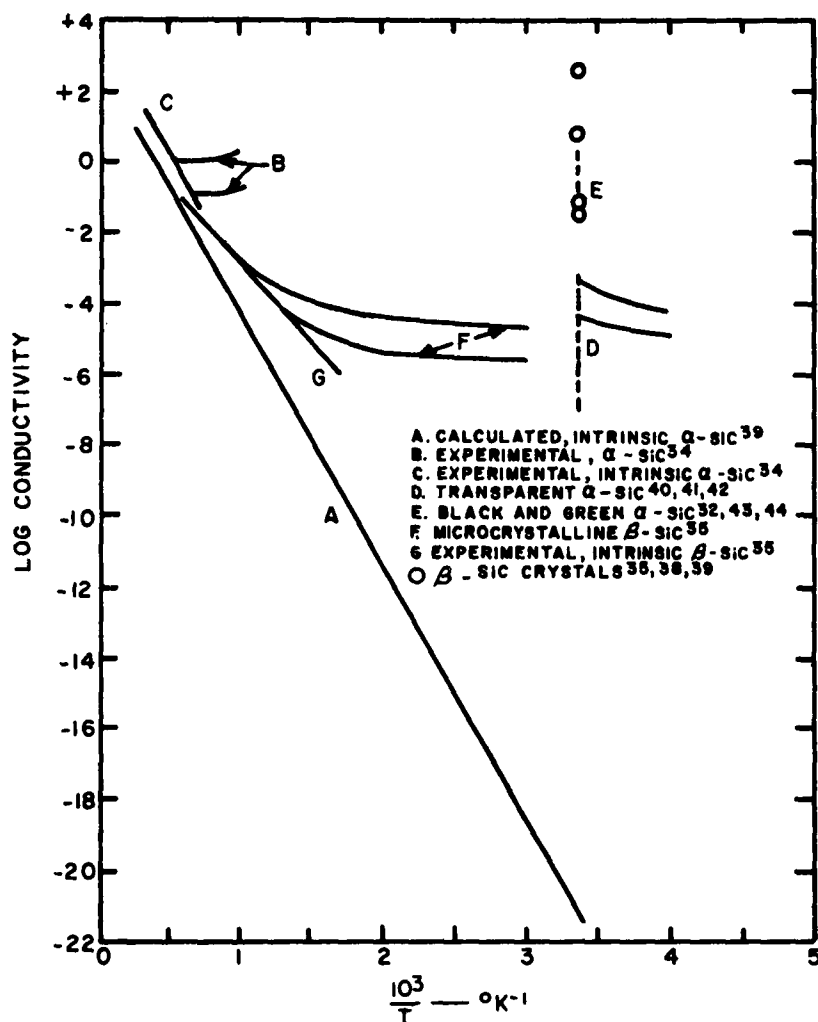


Figure 24. Electrical Conductivity of Silicon Carbide

Since the number of organizations engaged in the determination of the properties of silicon carbide is rather small, it was considered advisable to survey each organization's work and, in addition to the reporting of the results obtained, to include some of the most important techniques and equipment used.

Table II. Electrical Properties of β -SiC at 20° and 650°C

| Property | Value at 20°C | Reference | Value at 650°C | Reference |
|--|--|------------|-----------------------------------|-----------|
| Band Gap (E_g) | 2.86 ev | 30 | 2.66 ev | 51 |
| Electron Mobility (μ_n) | 100-140 cm ² /volt sec | 36 | 30 cm ² /volt sec | 51 |
| Hole Mobility (μ_p) | 10-25 cm ² /volt sec | 36 | 2 cm ² /volt sec | 51 |
| Lifetime of Electrons (τ_n) | 10 ⁻⁶ -10 ⁻⁸ sec | 32, 45 | 10 ⁻⁸ sec | 51 |
| Lifetime of Holes (τ_p) | 10 ⁻⁶ -10 ⁻⁷ sec | 46 | 10 ⁻⁸ sec | 51 |
| Diffusion Constant of Electrons (D_n) | 2 cm ² /sec | 32 | 2.4 cm ² /sec | 51 |
| Diffusion Constant of Holes (D_p) | 0.25 cm ² /sec | 37, 47 | 0.16 cm ² /sec | 51 |
| Electron Diffusion Length (L_n) | 5 μ | 32 | 1.6 μ | 51 |
| Hole Diffusion Length (L_p) | 5 μ | 32 | 0.4 μ | 51 |
| Effective Mass of Electrons (m_n^*) | 0.6 m_e | 32 | 0.6 m_e | 51 |
| Effective Mass of Holes (m_p^*) | 1.2 m_e | 32 | 1.2 m_e | 51 |
| Intrinsic Carrier Concentration (N_i) | | | 5.75 x 10 ¹² /cc | 51 |
| Dielectric Constant (K) | | | 9.01 x 10 ¹³ farads/cm | 51 |
| Dielectric Constant high freq (K_∞) | 6.7-7 | 32, 48, 49 | | |
| Dielectric Constant low freq (K_s) | 10.2 | 50 | | |

4. Hall and Resistivity Measurements

Emission spectrographic analyses and electrical resistivities of β -SiC crystals grown by Stanford Research Institute under contract NObsr-72772 are summarized in Table III. A comparison of the impurities of the starting materials and those presented in Table III indicated that the impurities in most cases result from either the graphite or the silicon powder used for crucible coating. All of these crystals were n-type.

Resistivity measurements were made with a four-point probe device constructed by passing 5-mil tungsten wires through a boron nitride block to provide spacings of 0.28 millimeter. The probes were springloaded and electroetched to a fine point in a NaOH-H₂O solution. Because of difficulties encountered in obtaining good ohmic point contacts on silicon carbide, a slightly modified technique was adopted for these measurements. The voltage of the current supply to the outer probes was swept by a sawtooth voltage, and the current flowing through the crystal was measured by applying the voltage drop developed across a small resistor in series with the crystal to the horizontal deflection plates of an oscilloscope. The voltage appearing across the inner probes was applied to the vertical deflection plates, and the resistivity of the crystal could be determined from the slope of the current versus voltage curve thus plotted on the oscilloscope. The advantage of this method is that any contact problem becomes apparent immediately as a nonlinear voltage-current plot. A diagram of the experimental arrangement is shown in Figure 25.

The results of resistivity measurements as a function of temperature are shown in Figure 26. None of the crystals exhibited large resistivity changes with temperature.

Hall measurements on crystals containing 30 parts per million of boron indicated a resistivity of 0.10 ohm-centimeter and a Hall coefficient of 0.55 cubic centimeter per coulomb, giving a mobility of 5.5 square centimeters per volt second. Minority carrier lifetime measurements performed on crystals from runs number 51 and 58 (Table III) indicated a lifetime of 2.5×10^{-9} seconds for the pure material (run number 58).

Tyco Laboratories, Incorporated,⁵² used the electroless nickel technique (modified by sintering for 20 minutes in hydrogen at 840°C after ultrasonic cleaning) to prepare low-resistance ohmic contacts to SiC to conduct Hall measurements. The contacts were checked by viewing the current-voltage behavior on an oscilloscope. Figure 27

Table III. Emission Spectrographic Analyses and Electrical Resistivities of β -SiC Crystals

| Run Number | Crystal Color | Fe | Al | Impurities (ppm)* | | | | Mo | Ti | Resistivity (ohm-cm) | Remarks |
|------------|---------------|----|-----|-------------------|----|----|-----|-----|----|----------------------|--|
| | | | | Mg | Cu | Ca | B | | | | |
| 6A | Yellow-Green | 20 | 5 | <3 | <3 | -- | <15 | -- | -- | 0.015-20 | High density graphite |
| 7A | Green | | | | | | | | | 0.01-0.02 | High density graphite |
| 10A | Green | | | | | | | | | | High density graphite |
| 12A | Green | 70 | <5 | 60 | 8 | -- | 45 | -- | -- | | High density graphite |
| 18B | Green | -- | 5 | -- | -- | -- | -- | -- | -- | | UF4S Graphite |
| 19B | Yellow | -- | -- | -- | 2 | -- | -- | -- | -- | | UF4S Graphite |
| 20B | Yellow | -- | <5 | <3 | 4 | <4 | -- | <30 | -- | | UF4S Graphite; poor vacuum |
| 44 | Green | -- | -- | -- | <3 | 4 | -- | -- | -- | | UF4S Graphite |
| 45 | Black | -- | -- | -- | -- | 4 | -- | -- | -- | | UF4S Graphite; Argon atmosphere |
| 48 | Green | | | | | | | | | 0.03 | UT6 Graphite |
| 49 | Yellow-Green | -- | <5 | <3 | <3 | <4 | -- | <30 | 12 | | UT6 Graphite |
| 51 | Pale Yellow | -- | -- | <8 | -- | -- | -- | -- | -- | 0.03 | UF4S Graphite; first vacuum of 10^{-6} ; use of clean box in coating; Linde molecular sieve for gas purification |
| 52 | Yellow-Green | -- | -- | 10 | 5 | -- | -- | -- | -- | | UF4S Graphite |
| 53 | Yellow-Green | -- | -- | <3 | 2 | -- | -- | -- | -- | 0.03 | UF4S Graphite |
| 54 | Yellow-Green | | | | | | | | | 0.005 | UF4S Graphite |
| 55 | Yellow-Green | -- | -- | <3 | <2 | -- | -- | -- | -- | 0.02 | UF4S Graphite |
| 58 | Pale Yellow | -- | -- | -- | -- | -- | -- | -- | -- | 0.03-0.08 | UF4S Graphite; final coating technique |
| 59 | Yellow-Green | -- | -- | <3 | <2 | -- | -- | -- | -- | 0.02-0.03 | UF4S Graphite |
| 60 | Black | -- | -- | <3 | <2 | <4 | 190 | -- | -- | > 10^6 | UF4S Graphite; 1% B |
| 61 | Brown | -- | -- | <3 | <2 | -- | 30 | -- | -- | 0.1 | UF4S Graphite; 0.1% B |
| 63 | Yellow | | | | | | | | | 0.08-0.11 | UF4S Graphite; 0.1% Al |
| 64 | Green | -- | 260 | <3 | <2 | <4 | -- | -- | -- | 0.02 | UF4S Graphite; 1% Al |
| 65 | Yellow-Green | | | | | | | | | 0.02-0.03 | UF4S Graphite; 0.1% Fe |
| 66 | Yellow-Green | | | | | | | | | 0.02-0.05 | UT6 Graphite; 0.1% Sb |
| 67 | Yellow | -- | -- | <3 | <2 | -- | -- | -- | -- | 0.02-0.03 | UF4S Graphite; 1% Fe |
| 68 | Yellow | -- | -- | <3 | <2 | -- | -- | -- | -- | | UT6 Graphite (purified); 1% Sb |
| 69 | Yellow-Green | -- | -- | <3 | <2 | -- | -- | -- | -- | | UT6 Graphite (purified); 0.1% Cu |

* Values quoted = a factor of 5

-- Denotes that concentration of element was too low to be detected

< Denotes that trace quantities are suspected

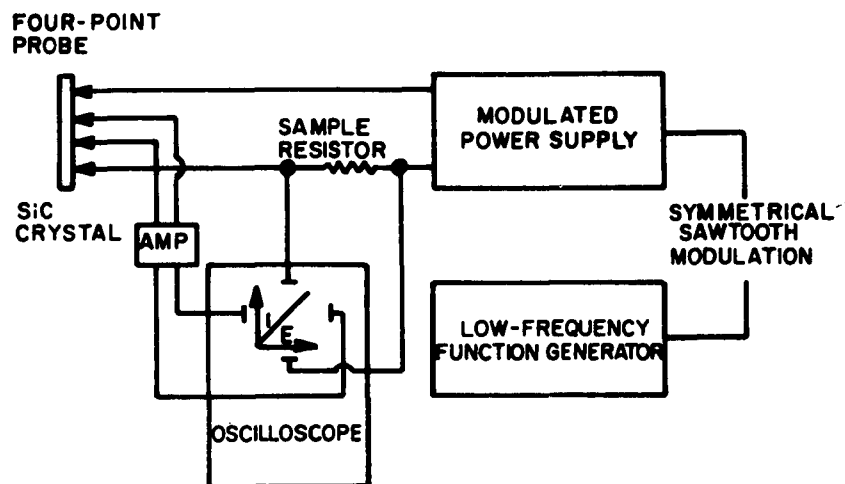


Figure 25. Sweep Method for Resistance Measurement

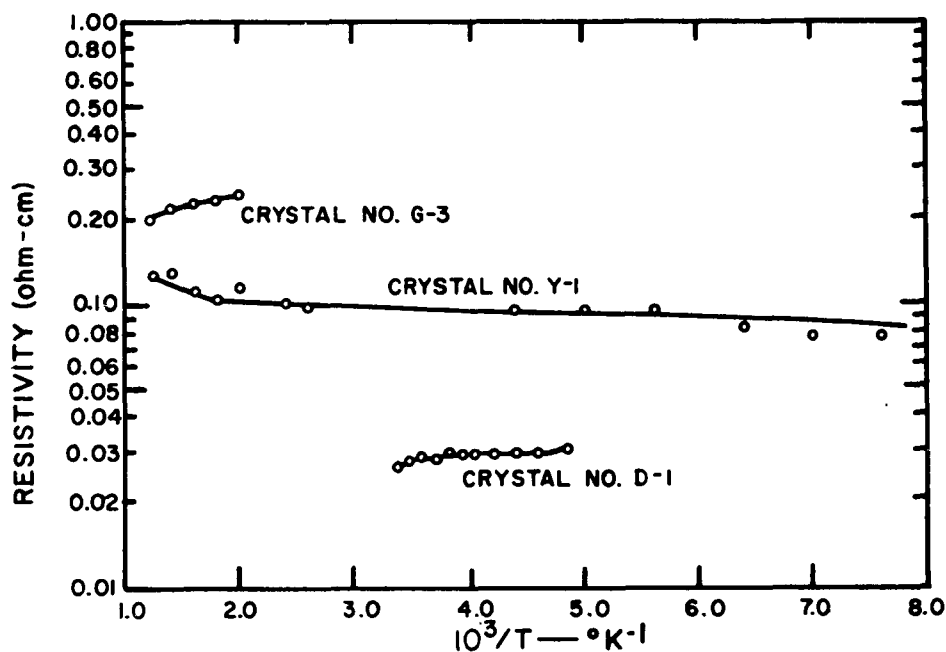


Figure 26. Electrical Resistivity Versus $10^3/T$ for β -SiC Crystals

shows such a curve both before and after sintering of the nickel. It can be seen that the current-voltage plot is linear in the low current range, but tends to become nonlinear at higher currents. A technique developed by Tyco Laboratories for the measurement of Hall coefficient

makes it unnecessary to measure explicitly either the magnetic field or the current through the sample. This is done by wiring the current leads to a calibrated Hall effect device in series with the current leads of the sample under test. The Halltron is mounted to the sample by taping it to the back of the Plexiglas frame shown in Figure 28. This frame holds the SiC disc and provides the contacts to it by means of four brass rods tipped with indium.

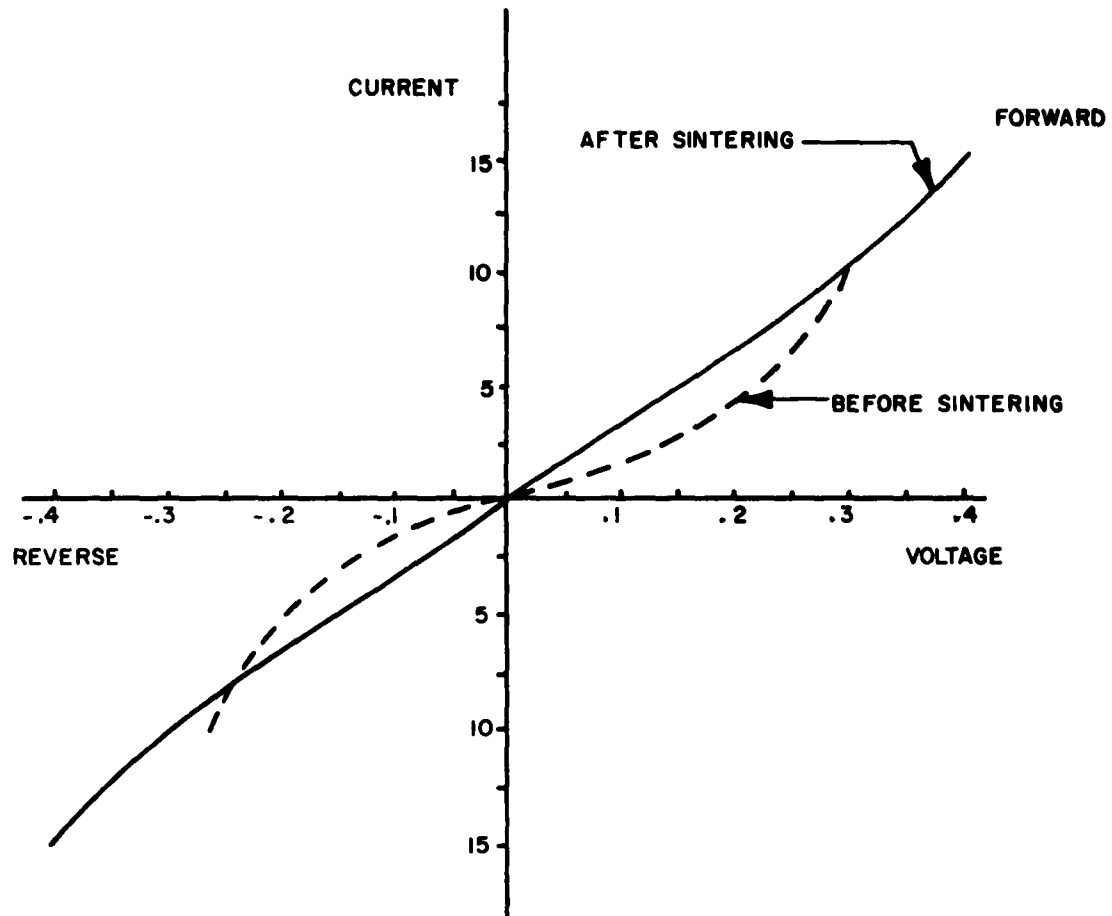


Figure 27. Current-Voltage Characteristics of Nickel Contacts to SiC

Since the planes of the Halltron and of the sample are parallel to each other, the magnetic field orthogonal to the current flow is identical. Further, since the current passes through both devices in series, and since the Hall voltage measured on the standard is a function of the

product of current and magnetic field, it is not necessary to measure the current and the field separately.

The following values were obtained by Tyco Laboratories on p-type SiC:

resistivity - 0.51 ohm-centimeter

mobility - 7.4 centimeter² per volt second

carrier concentration - 1.6×10^{18} per cubic centimeter.

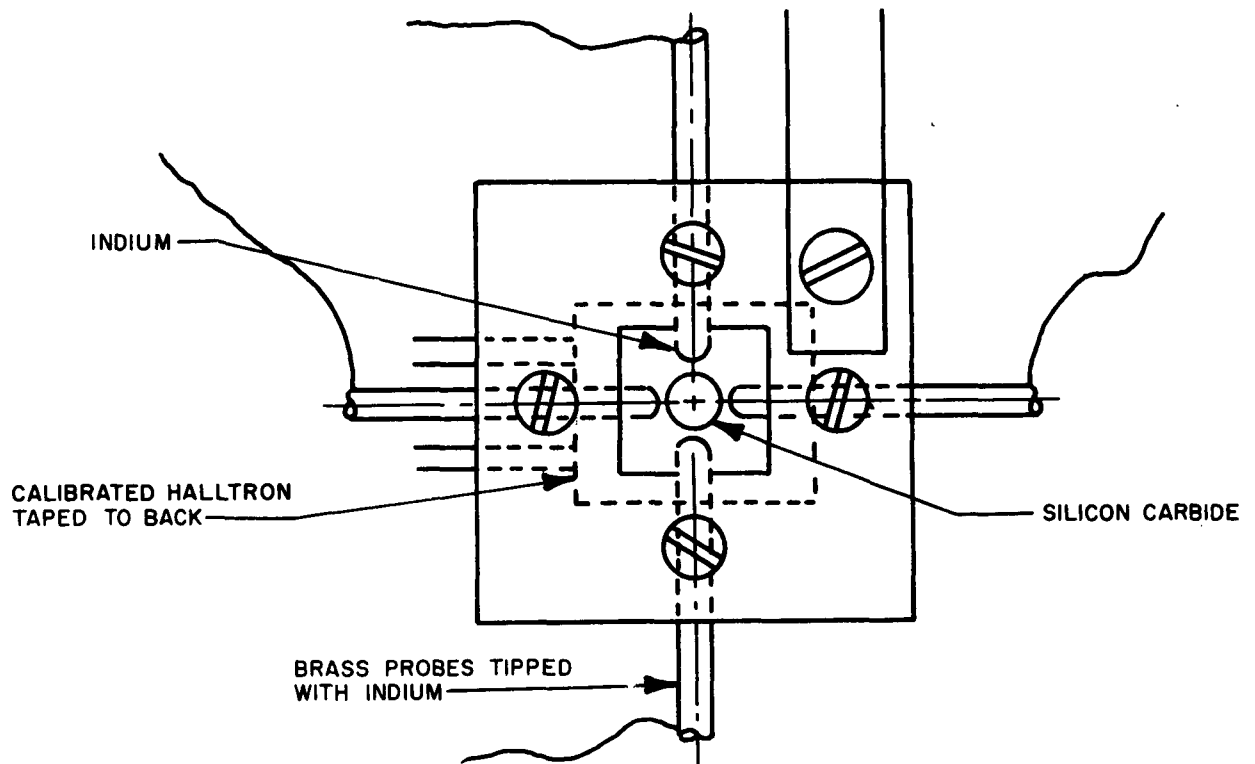


Figure 28. Jig for Holding SiC Disc in Position for Hall and Resistivity Measurements

5. Spectral Transmission

Spectral transmission curves measured on a thin β -SiC plate and a colorless α -SiC crystal are shown in Figure 29.²⁵ It can be seen that the cutoff region was quite broad for the β -SiC crystal. The shallow slope of the band edge observed in β -SiC makes estimation of its optical band difficult.

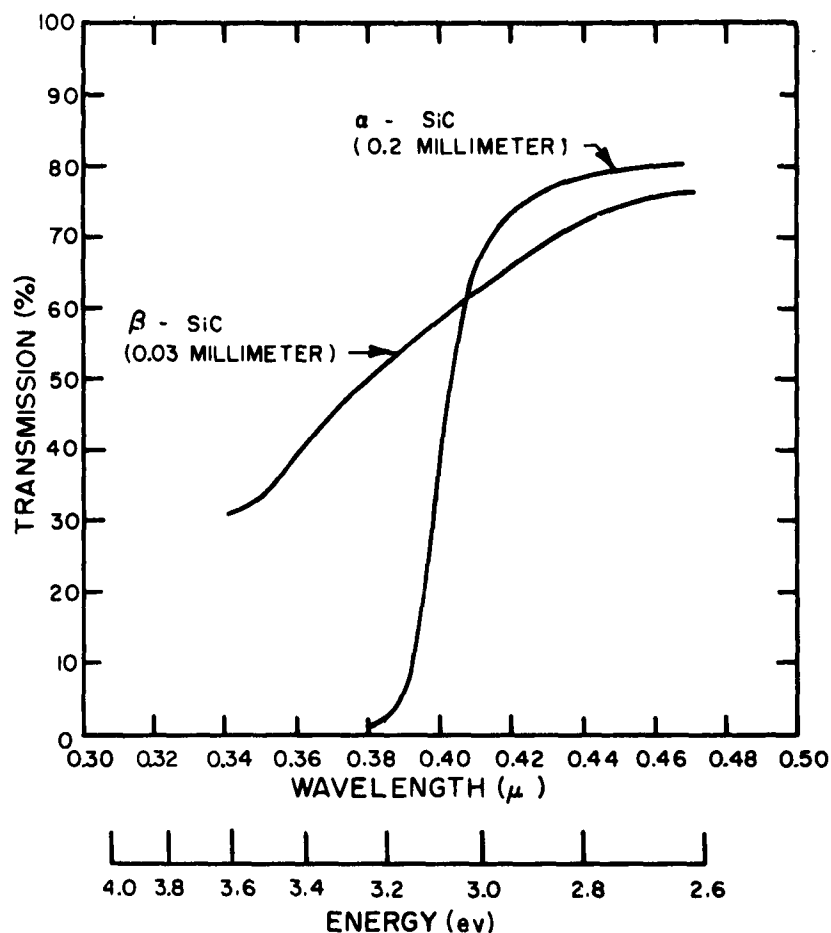


Figure 29. Spectral Transmission of Silicon Carbide Crystals at Room Temperature

Raytheon⁵³ measured transmission spectra on a recording single-beam spectrometer. A tungsten lamp was used as a light source and the dispersing element was a double-prism Leiss monochromator using flint glass prisms. An RCA 7265 photomultiplier tube, powered by a Northeastern regulated high-voltage supply, was used as detector. Chopped-beam operation was used, employing a Perkin-Elmer Model 107 13-cycle amplifier. The average resolution was 0.005 electron volts over the spectral range studied.

Transmission measurements were made using the conventional sample-in, sample-out method. A resistance-heated, evacuated, copper sample holder was placed between the monochromator exit slit and the detector. A Wheelco Instrument Capacitrol was used for temperature regulation, and iron-constantan thermocouples were used for both measurement and control. The temperature during recording of any spectrum varied by no more than $\pm 1^\circ\text{K}$ and the values quoted are estimated to be accurate to $\pm 2^\circ\text{K}$.

Each transmission spectrum was taken twice at each temperature. The transmission was determined at several wavelengths by linear interpolation between the wavelength markers, using a Gerber scale. An average value of the transmission was then calculated at each wavelength. Transmission spectra were taken at 295°, 351°, 400°, 499°, 550°, 601°, 652°, and 700°K. These spectra are shown in Figure 30. The values of transmission obtained are estimated to have an uncertainty of ± 3 percent for transmissivity values less than or equal to 0.40; the results, as can be seen, have more scatter for higher values of transmission.

Because of the scattering at high transmission, absorption coefficients, although calculated, do not add significantly to the interpretation of the data, and isotransmission plots are presented. It is apparent that deriving a temperature dependence of the edge from isotransmission curves is the same as that obtained from an isoabsorption plot if it is certain that the shape of the absorption curve does not change as a function of temperature.

Of most significance is the slope of the isotransmission as the absorption approaches zero, since high transmission corresponds to the edge of the band gap itself. Hence, for the most accurate determination of dE_G/dT by this method, the transmission should be measured to its maximum value, i. e., into the flat region of the transmission curve. It is this region which unfortunately presents scatter of the data (Figure 30). The region of lower transmission ($T \leq 0.40$) consists of a series of curves whose shape is not changing with temperature. A measurement of the slope of isotransmission data taken from this region therefore gives an indication of the temperature dependence of the gap, the accuracy of the value being dependent on the validity of the assumption of no shape change.

The isotransmission plot consists of parallel straight lines for the range of transmission plotted. This is seen in Figure 31, in which the isotransmission lines are parallel to within ± 3 percent and the slopes show no trend as a function of transmission. The average value of the slope of the isotransmission lines shown in this figure is $(-5.8 \pm 0.2) \times 10^{-4}$ electron volt per degree K over the temperature range 295°K to 700°K.

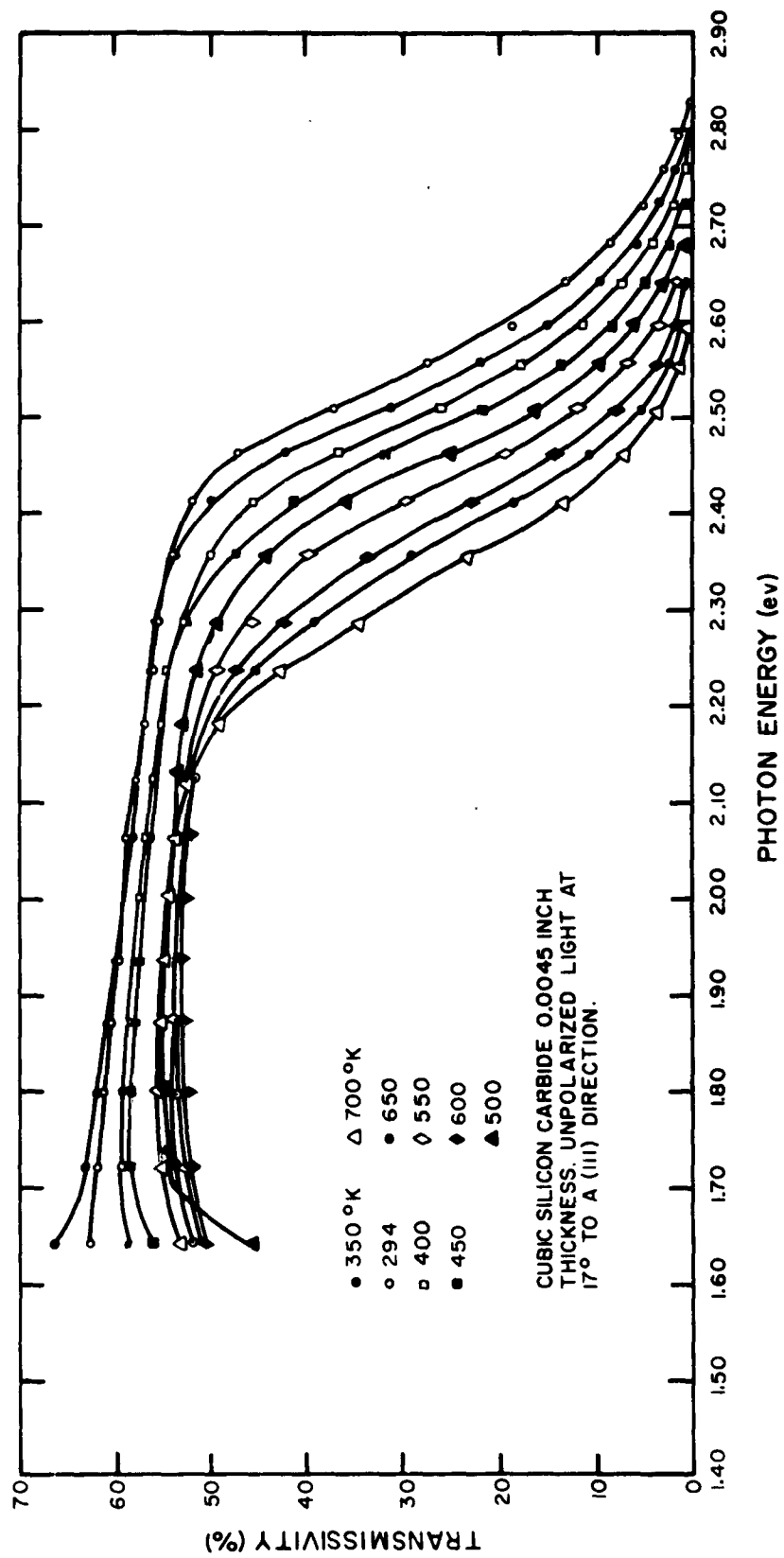


Figure 30. Transmission Spectra of Cubic Silicon Carbide

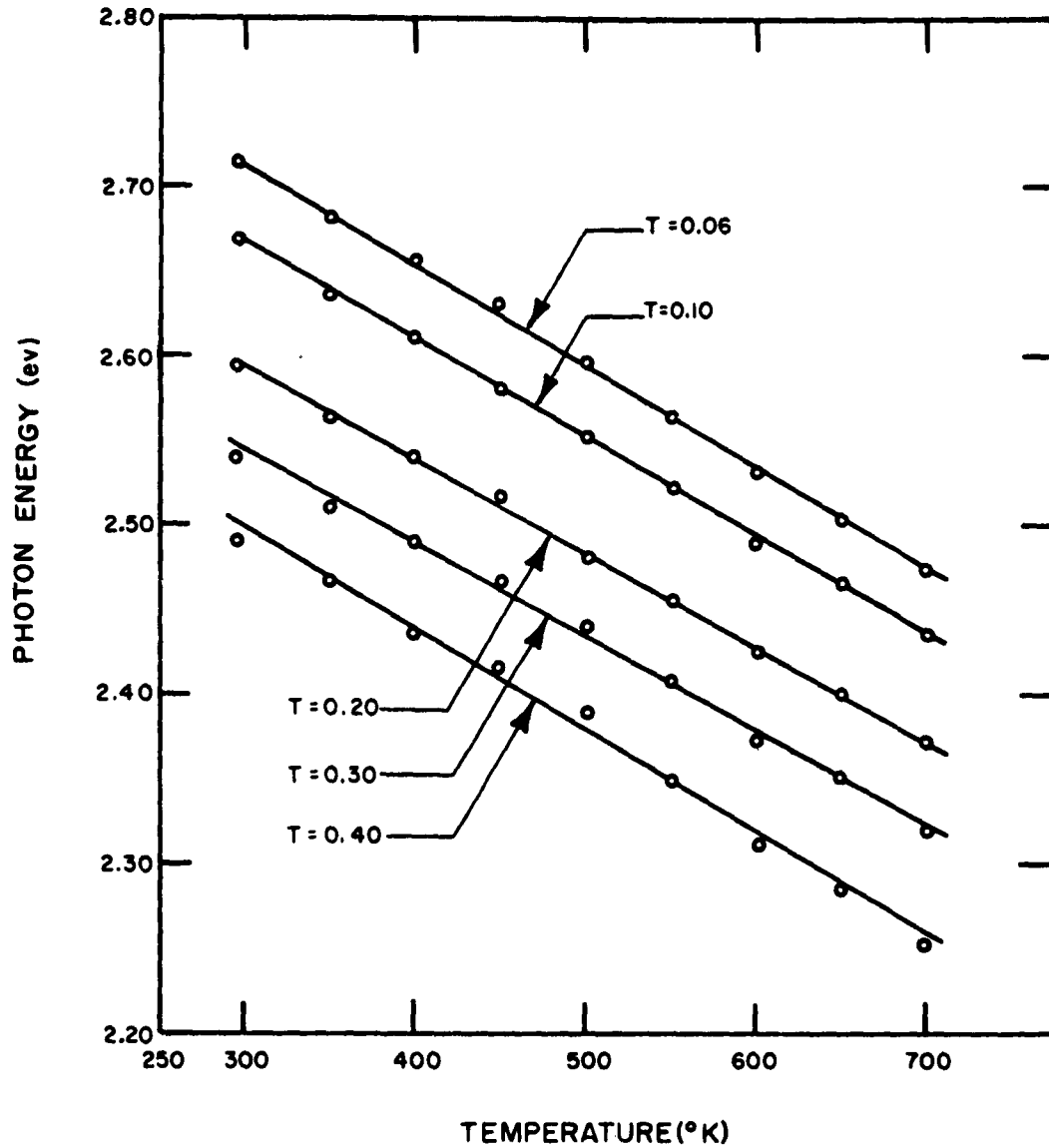


Figure 31. Isotransmission Plot for $T \leq 0$

6. Refractive Index

Raytheon measured the ordinary refractive index, n , of a sample of hexagonal silicon carbide of unknown polytype. By measuring transmission interference fringes in the spectral region from 3800 Å to 7700 Å, the relation $p\lambda = 2nt$ could be used to determine n . In this equation, p is the order number of an interference maximum, λ the

wavelength, t the sample thickness, and n the refractive index. The order numbers p were assigned by extending the measurements to about 4 microns, where p is small. A plot of n versus λ is shown in Figure 32. There is no explanation for the peaks at approximately 5500 Å and 6300 Å.

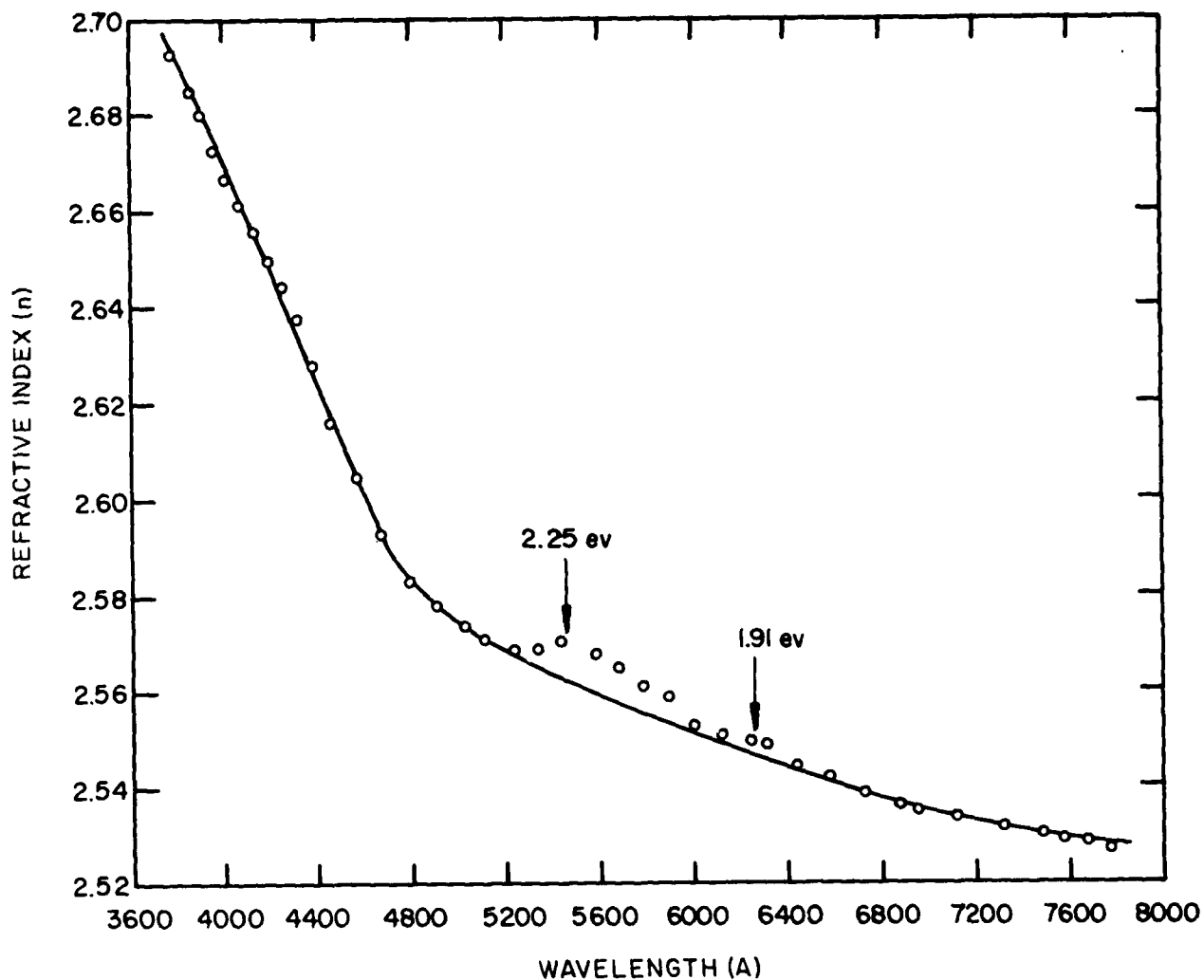


Figure 32. Ordinary Refractive Index for Hexagonal Silicon Carbide

7. Reflectivity

The specimens (supplied by the Exolon Corporation) were of α -II SiC, transparent or green in color, pyramidal in form, about 3 millimeters high, and often larger than 25 millimeter² in basal area. The solid curve in Figure 33 gives the reflectivity, measured at near

normal incidence, of a grown (0001) surface of α -II SiC. The dashed curve in the same figure shows the reflectivity from the same sample when the grown surface has been ground and polished. The grinding and polishing is done by using diamond abrasives on copper plates. The two curves are the same at short and long wavelengths but differ considerably within the reflectivity band. When the polished surface was oxidized for 2 hours at 1000°C, the specimens exhibited the reflectivity shown by the third curve in the same figure.

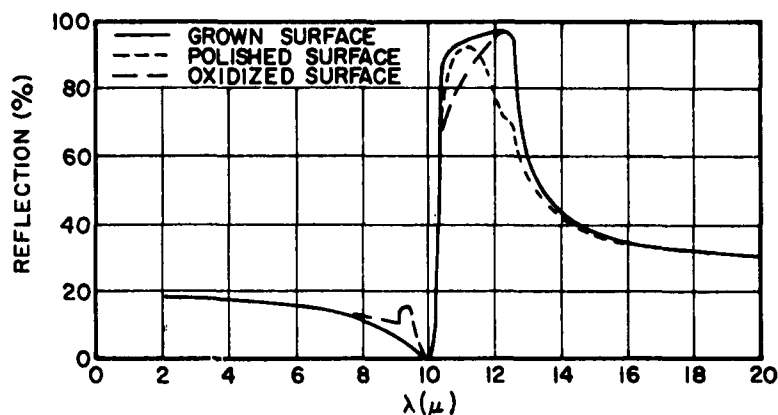


Figure 33. Ordinary Ray Reflectivity

8. Photoluminescence 55

β -SiC exhibits photoluminescent properties. More than 20 percent of the 125 different crystal batches tested by Stanford Research Institute displayed some degree of photoluminescence at 77°K, when viewed under ultraviolet radiation. Varying intensities of orange, pink, red, and green colors were observed. Crystals from very pure runs, boron-doped crystals, and impurity-laden crystals were not photoluminescent. Aluminum-doped, high-purity crystals displayed the strongest photoluminescence, emitting spectacularly intense orange or pink light that could be seen even in a brightly lit room. In the dark, these crystals appear as small brightly-glowing coals.

The relationship between resistivity, purity, and photoluminescence in crystals of β -SiC was tabulated by Stanford Research Institute in order of decreasing luminescence intensity for a number of crystal batches and is reproduced in Table IV. At liquid nitrogen temperature, every crystal in luminescing batches emitted light. Some crystals in a limited number of batches luminesced under ultraviolet light at room temperature.

Table IV. Photoluminescence Versus Purity and Resistivity of β -SiC

| Run No. and crystal type | Luminescence at 77°K | | | Luminescence at room temperature | |
|-----------------------------|--|------------------------------|-------------------------|---------------------------------------|---------------------------|
| | Brightness and color | Purity (ppm) | Resistivity (ohm-cm) | Color | % Crystals luminescing |
| 113 n | Brilliant Orange | <10 Al | 10^3 | Yellow | 75 |
| 124 p-n | Brilliant Pink | 0-10 Al | | None | |
| 111 p | Brilliant Pink | <10 Al | 10 | None | |
| 63 n | Bright Orange | + N ₂ 40 Al | 10^{-1} | Dull Red | 100 |
| 20 n | Bright Pink | 5 Al 30 Mo+N ₂ | 10^{-2} | Yellow | 15 |
| 64 n | Orange | 250 Al + N ₂ | 10^{-1} | Dull Red | 90 |
| 112 n | Pink | 5 Mg | 1-10 | None | |
| 125 n | Orange | Nil | 1-10 | Green, Yellow, Red | 25 |
| 100 n | Dull Orange | Nil | 4-10 | Yellow, Red, Green | 25 |
| 114 n | Dull Orange | Nil | 1-10 | Yellow and Green | 75 |
| 110 p | Very Dull Green, Pink, Yellow | 200 Al | 10^{-1} | None | |
| 104 n | Very Dull Red | < 5 Ca | 1-10 | Dull Red | 75 |
| 117 n | Very Dull Orange | <10 B | 10^3 | Bright Yel- low, Red, and Green | 30 |

A few crystals in some batches (runs number 20, 110, 111, and 113) show green luminescence at 77°K. These crystals, when taken from the yellow-colored crystal batches, were usually found to be white transparent, light green, or colorless. Some of these crystals, according to X-ray studies, have a hexagonal crystal structure similar to type II α -SiC. Apparently, under special conditions, crystals of α -SiC may be grown at temperatures as low as 1450°C.

9. Optical Absorption ⁵⁶

Philipp and Taft measured the optical absorption of single crystal SiC in both the cubic and hexagonal modifications. Absorption coefficients are shown in Figure 34. These values were determined by direct measurement of transmission on polished samples. Above 10^3 centimeter⁻¹, the curves nearly coincide. At long wavelengths, the cubic crystal shows the stronger absorption.

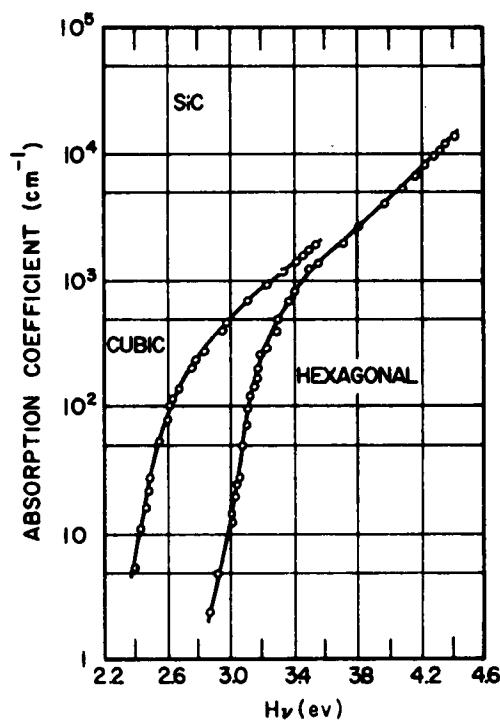


Figure 34. Absorption Spectra of Cubic and Hexagonal, Type 6H, Silicon Carbide at 300°K

10. Oxidation

It is well known that the electrical and chemical properties of semiconductor surfaces can be drastically affected by even small fractions of an absorbed monolayer. Dillon⁵⁷ studied the interaction of oxygen with SiC surfaces in high-vacuum and high-pressure environments, and the results may be summarized as follows:

At low pressures and room temperatures, oxygen is absorbed with a sticking coefficient of the order of 0.01 on a cleaned SiC surface. The exact structure of the absorbed layer has not been specified, but it is probably no more than two monolayers thick. The presence of this absorbed layer results in large changes in such surface properties as the work function and the photoelectric yield.

As the temperature is increased and the oxygen pressure is maintained below 10^{-1} millimeter of mercury, SiC vaporizes in the form of volatile oxides resulting in detectable weight losses. If oxidation takes place at pressures of the order of one atmosphere and temperatures above 900°C , films of SiO_2 , hundreds of monolayers thick, can be formed. Experiments indicated that SiO_2 films acted merely as a resistive layer.

Jorgensen, et al,⁵⁸ studied the rate of oxidation of SiC in an atmosphere of dry oxygen between the temperatures of 900° and 1600°C , using a thermogravimetric apparatus, which allowed a continuous measurement of weight gain versus time. The apparatus (Figure 35) consisted of helical silica glass spring, Gaertner cathetometer, and an electric furnace heated by Kanthal-Super elements. The powdered sample was placed in a porous alumina crucible and suspended from the silica spring by an alumina rod. The rate of oxidation was found to be diffusion controlled. A plot showing the percent of oxidation as a function of time at different temperatures is shown in Figure 36.

Other investigators who studied the oxidation of SiC include Adamsky, Lambertson, and Nowak.⁵⁹ Adamsky oxidized powder samples of α -SiC type II after a preliminary outgassing at 1300°C for 16 hours and at a pressure of 1.5×10^{-3} millimeters of mercury. The oxidation rate was measured as the determination of the CO and CO_2 produced, and checked by determination of the SiO_2 formed on the surface of the powder.

Lambertson investigated oxidation over a wider temperature range and found that, at temperatures up to 950°C , the oxidation is very slow. From 950° to 1600°C the oxidation is diffusion controlled, but above 1650°C it becomes again reaction controlled with the reaction between SiC and SiO_2 as the rate-controlling step.

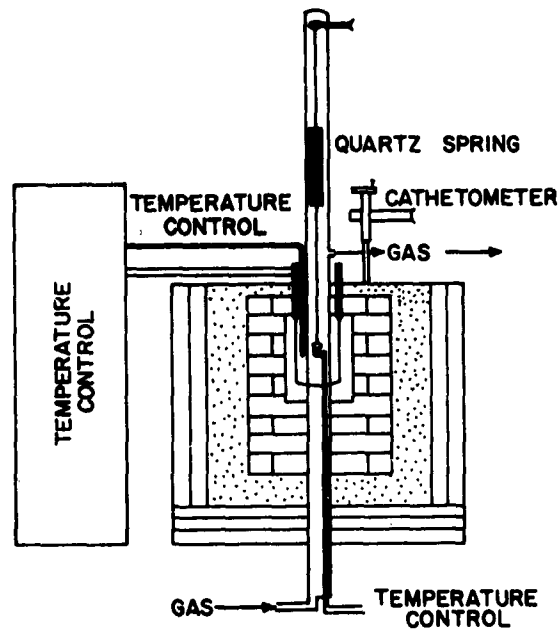


Figure 35. Thermogravimetric Apparatus

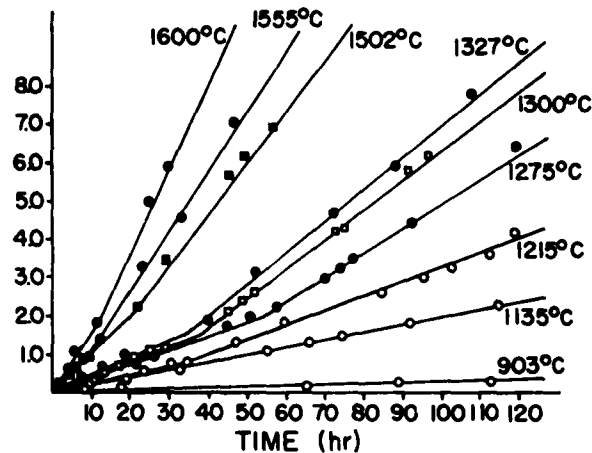


Figure 36. Percent of Oxidation, Allowing for Change in Area, Versus Time

Using extended refractory bodies (as opposed to powder), and working at 1550°C in a flow of oxygen of about 1 liter per minute, Nowak investigated the oxidation of refractory materials including SiC. He reported that an alloy of SiC:B₄C was the most highly resistant to oxidation of a series of materials including recrystallized SiC, SiC-coated graphite, ZrC, and TaC. The results of the tests on recrystallized SiC are shown in Figure 37.

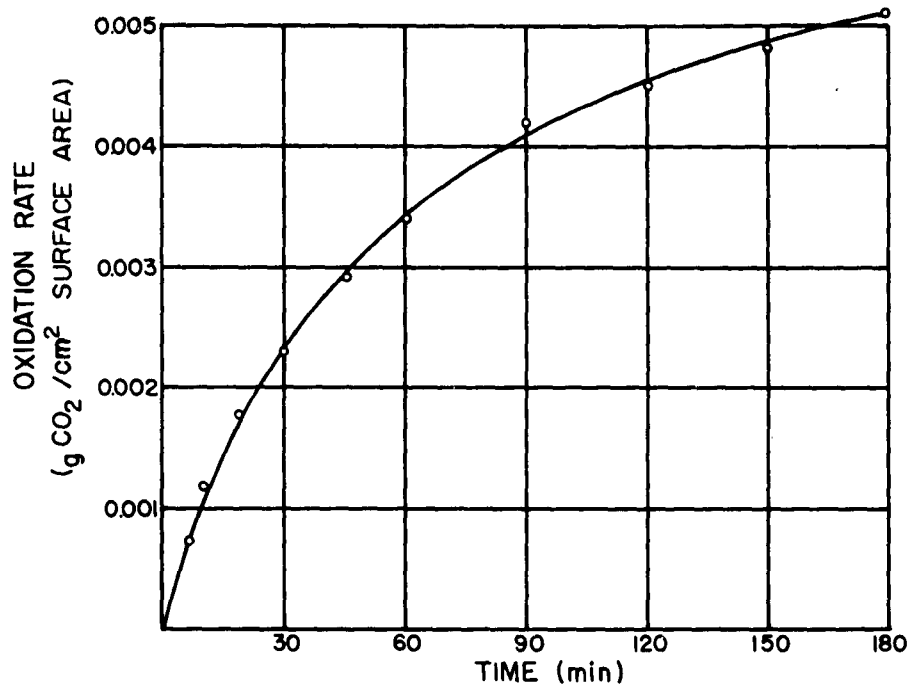


Figure 37. Oxidation of Silicon Carbide

11. Effects of Radiation on Silicon Carbide ⁶⁰

Primak investigated the radiation-induced expansion of silicon carbide by irradiating specimens of hexagonal SiC in a nuclear reactor. Specimens were irradiated for about 1.08×10^{20} and 1.80×10^{20} damaging neutrons per centimeter². From these experiments, the fractional expansions along the optic axis and perpendicular to it were calculated and were found to be in the ratio of 0.97 for both irradiations. The results of these experiments are summarized in Table V.

Table V. Results of SiC Sample Irradiation

| Specimen Number | L_0 (10^{-2} in.) | ΔL (10^{-4} cm) | γ (10^{-4}) | ρ (g^5/cm^3) | δ (10^{-4}) |
|-----------------|---------------------------|-------------------------------|---------------------------|--------------------------|---------------------------|
| 1 | | | | 3.2148 | |
| 2 | 5.06 | 9.09 | 70.7 | 3.1469 | 216 |
| 3 | 4.26 | 7.81 | 72.2 | 3.1462 | 218 |
| 4 | 3.04 | 5.49 | 71.1 | 3.1455 | 220 |
| 5 | 4.81 | 11.33 | 93.0 | 3.1228 | 295 |
| 6 | 4.20 | 9.85 | 92.4 | 3.1231 | 294 |
| 7 | 4.82 | 12.15 | 99.0 | 3.1232 | 293 |

Specimen number 1 was not irradiated because it was used as a standard. Specimens number 2 through 4 received 1.08×10^{20} damaging neutrons per centimeter², and specimens number 5 through 7 received 1.80×10^{20} damaging neutrons per centimeter². In the above table, (LO) stands for original length, (ΔL) for radiation-induced expansion, (γ) for fractional expansion parallel to the optical axis, (ρ) for density, and (δ) for dilation.

On progressive annealing after irradiation, the dilation disappeared. Figure 38 shows the fraction of the original dilation of an irradiated commercial black SiC remaining after successive annealings.

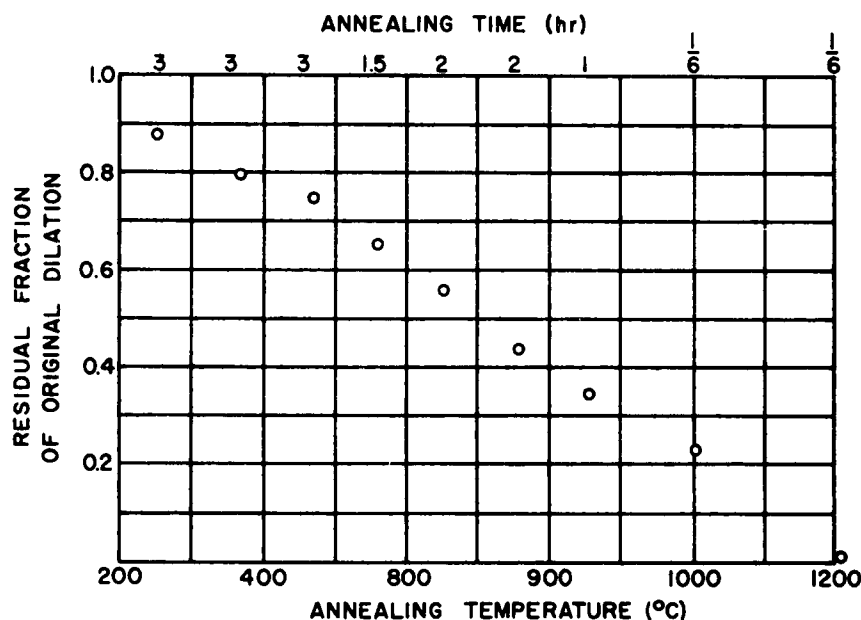


Figure 38. Fraction of Original Dilation of an Irradiated SiC Sample Remaining After Successive Annealings

12. Specific Heat⁵⁹

Several values of the specific heat of SiC as a function of temperature are given in Table VI.

13. Thermal Conductivity⁵⁹

Values of thermal conductivity obtained from different sources are presented in Table VII. As with other properties, there appears to be considerable variation in the values obtained by different investigators. All of the values in this table show that the thermal conductivity is inversely proportional to the temperature

Table VI. Specific Heat of Silicon Carbide

| Temperature (°C) | * cal ^s °C ⁻¹ mole ⁻¹ | | | | |
|------------------|--|-------|-------|-------|-------|
| | a | b | c | d | e |
| 0 | 5.61 | - | 5.87 | 5.63 | - |
| 27 | - | - | 6.60 | 6.42 | 6.46 |
| 200 | 9.34 | 8.98 | 9.00 | 8.97 | - |
| 327 | - | - | 9.85 | 9.88 | 10.06 |
| 400 | 11.10 | 9.72 | 10.22 | 10.27 | - |
| 600 | 11.0 | 10.45 | 11.06 | 11.15 | - |
| 627 | - | - | 11.16 | 11.25 | 11.21 |
| 800 | 9.01 | 11.18 | 11.76 | 11.88 | - |
| 927 | - | - | 12.18 | 12.32 | 11.98 |
| 1000 | 4.93 | 11.90 | 12.42 | 12.56 | - |
| 1200 | - | 12.64 | - | - | - |
| 1227 | - | - | 13.13 | 13.29 | 12.65 |
| 1400 | - | 13.36 | - | - | - |

*Columns a, b, c, etc. represent values obtained by different investigators

Table VII. Thermal Conductivity of Silicon Carbide

| Temperature (°C) | K cgs | | | | |
|------------------|-------|------|-------|-------|-------|
| | a | b | c | d | e |
| 200 | - | - | 0.12 | - | 0.244 |
| 400 | - | - | 0.095 | - | 0.172 |
| 500 | 0.08 | - | - | - | - |
| 600 | 0.07 | - | 0.073 | 0.25 | 0.138 |
| 800 | 0.055 | - | 0.062 | 0.18 | 0.115 |
| 1000 | 0.05 | - | - | 0.12 | 0.101 |
| 1100 | - | 0.03 | - | 0.093 | - |
| 1200 | - | - | - | 0.072 | - |
| 1400 | - | - | - | 0.043 | - |
| 1500 | - | - | - | 0.033 | - |

14. Thermal Expansion ⁵⁹

Table VIII gives several values (a, b, c, etc.) obtained by different investigators for the mean value of the linear thermal expansion of SiC for the temperature range from 25°C to the temperature in column one of the table.

Table VIII. Linear Thermal Expansion of SiC

| Temperature Range 25°C to ____°C | $\alpha^{-1} \times 10^6$ | | | | | | | |
|--|---------------------------|------|-----|-----|------|------|------|------|
| | a | b | c | d | e | f | g | h |
| 200 | 3.37 | 3.26 | - | - | 4.4 | - | - | - |
| 300 | - | - | 3.8 | 3.6 | - | - | 3.69 | 2.95 |
| 400 | 4.26 | 4.05 | - | - | 4.7 | - | - | - |
| 600 | 4.36 | 4.29 | 4.3 | 4.7 | 5.0 | - | - | - |
| 800 | 4.57 | 4.52 | - | - | 5.06 | - | - | - |
| 900 | - | - | 4.5 | 4.9 | - | - | - | - |
| 1000 | 4.78 | 4.78 | - | - | 5.1 | 5.74 | 4.01 | 4.72 |
| 1200 | - | 5.00 | 4.8 | 5.1 | 5.14 | 5.62 | 3.91 | 5.04 |
| 1400 | - | 5.20 | - | - | 5.18 | 5.75 | - | - |
| 1500 | - | 5.48 | - | - | - | - | - | - |
| 1600 | - | - | 5.2 | 5.6 | 5.24 | 5.65 | - | - |
| 1800 | - | - | - | - | - | 5.75 | - | - |
| 2000 | - | - | - | - | - | 5.87 | - | - |
| 2200 | - | - | - | - | - | 5.79 | - | - |
| 2400 | - | - | - | - | - | 5.89 | - | - |

Section IV. PROCESSING OF SILICON CARBIDE FOR DEVICES

1. Formation of Junctions and Contacts

Practically all important phenomena which take place in solid-state devices, whether they are diodes, transistors, switching devices, or other active elements, take place at the junction or transition region between two different materials. There are three popular techniques used to make junctions: the fusion method, the diffusion method, and the grown method. In the fusion method, a piece of material of the type to be used for the base is first selected, and the surfaces are treated. Then a small piece of material of the opposite impurity type is placed on the surface, and the wafer is heated. In the diffusion process, a slab of material is heated to a high temperature and exposed to a gaseous impurity. This impurity diffuses slowly into the surface of the material. The concentration of the impurity is highest at the surface and decreases exponentially inward. The major portion of the original semiconductor slab is unchanged, but the surfaces become doped to the conductivity type of the impurity. A junction is thus formed directly under the surface. The grown junction, as the name implies, is formed during the crystal growing process.

a. Fusion^{61, 62, 63}

The fusion of alloys to semiconductors is used to produce either an ohmic bond for attaching the leads or to produce a p-n junction. Westinghouse Electric Corporation, under contract AF 19(604)-5997, studied extensively the fusion of silicon and platinum alloys. A controlled-atmosphere furnace (Figure 39), in which fusion of various alloys to silicon carbide can be accomplished at temperatures up to 2400°C, was designed and built. The base of the furnace is made of transite. The spindle of a micrometer is used as the support for the crystal and enables the crystal to be raised or lowered with respect to the heating element. The heating element (Figure 40) is a graphite strip with a thin central cross section. For high-temperature work, a spacer of molybdenum is placed on the upper end of the spindle, and a tungsten support is used on top of it. The crystal is then placed on top of this small tungsten wafer, and the assembly is positioned by use of the micrometer.

A temperature gradient is maintained across the crystal as the surface nearest the graphite boat is at a higher temperature than the one in contact with the metal support. After the maximum temperature of fusion has been reached, the crystal is slowly moved away from the boat by rotation of the spindle.

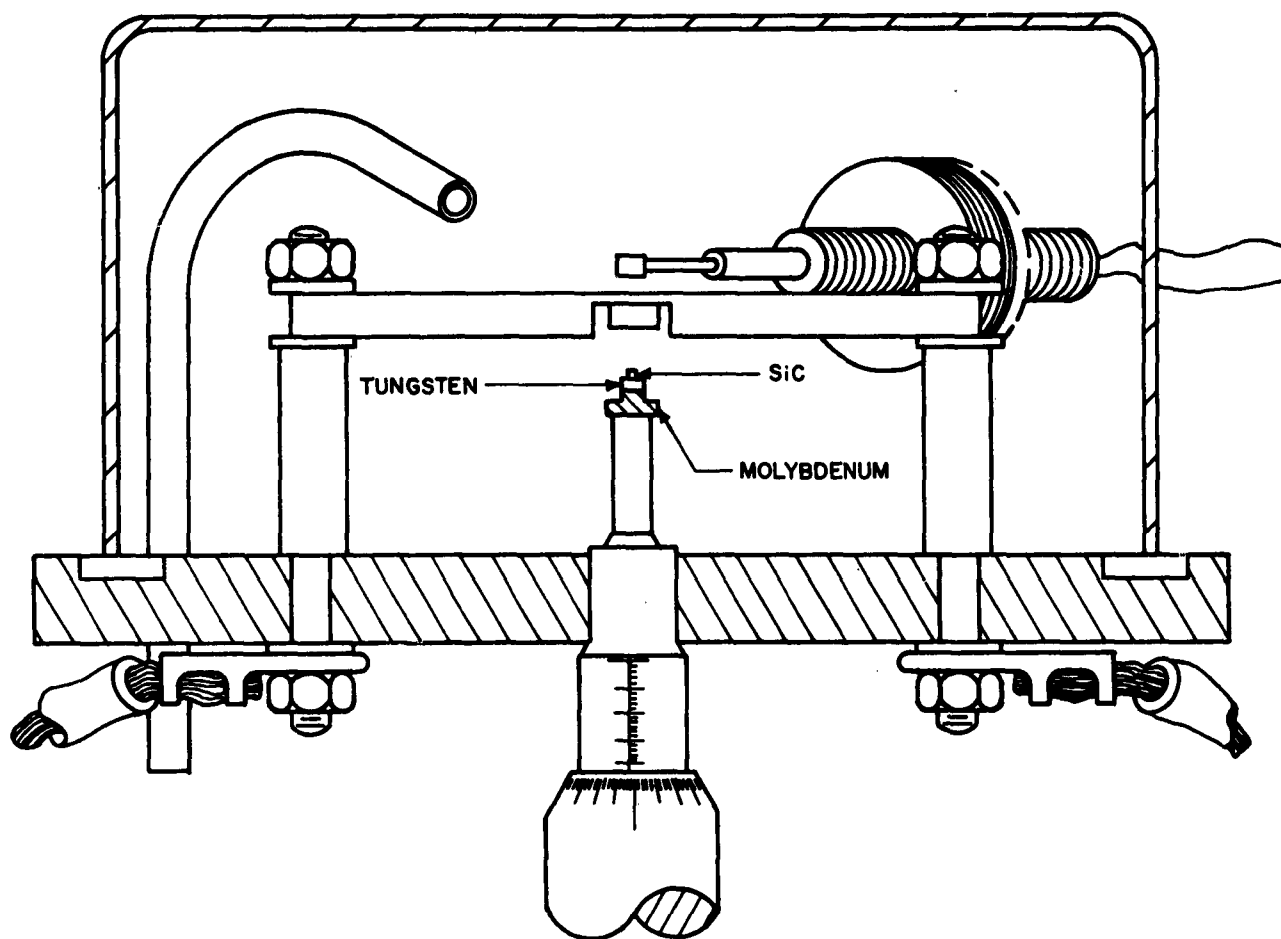


Figure 39. Fusion Assembly

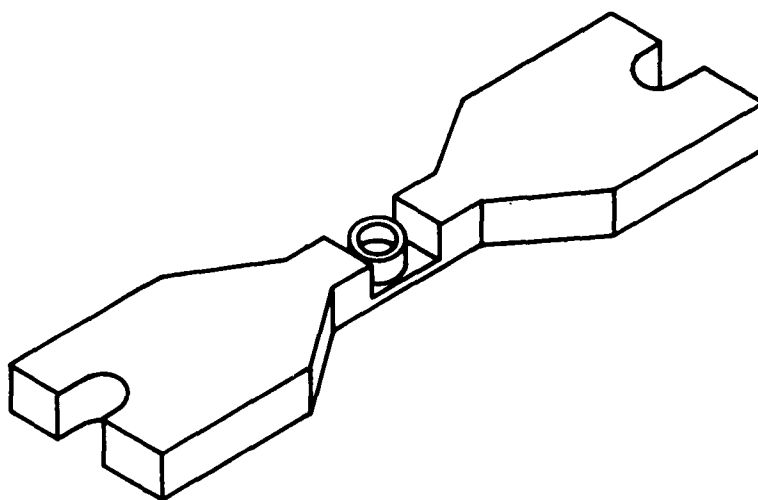


Figure 40. Heater Design for Fusion Experiments

Prior to fusion, samples of silicon carbide are selected and checked for resistivity and Hall effect measurements. All of the alloys tried by Westinghouse were made in the same manner. The elements were weighed and placed together in a small quartz crucible. The crucible was then positioned on a graphite heating strip, and the materials were melted in a vacuum. After the alloy was removed from the quartz crucible, it was flattened and rolled to a thickness of 2 to 3 mils. The alloy was then cleaned in aqua regia and stored for future use. Just before use, the alloy was cut into pieces of 0.0005 inch or less.

The crystal platelet was scribed and lapped. It was placed on top of a tungsten wafer, and a small drop of mineral oil was placed on the surface of the crystal. The freshly cut alloy was then placed in the drop of oil, and the whole assembly was loaded onto the molybdenum spacer. The spacer was then placed on the micrometer spindle, and raised until the top surface of the crystal was 0.005 inch from the under surface of the graphite boat. Then dry argon was allowed to flow for a few moments. Maximum furnace temperature could be reached in a few seconds. The assembly was held at that temperature for 20 seconds, during the last 15 of which the supporting spindle was lowered through one revolution (0.025 inch). The temperature dropped several hundred degrees in 5 seconds after the current to the boat had been turned off.

During the high-temperature treatment, the surface of the crystal is altered. The higher vapor pressure of silicon causes it to be driven off preferentially, leaving a very thick film of highly-conductive graphite. This film can be removed by oxidation in air, after which the crystals are ready for electrical testing.

b. Diffusion

The low mobility and short lifetime of minority carriers in silicon carbide present difficulties in the design and fabrication of silicon carbide transistors. It is necessary to maintain very close tolerances in the device structure and to control impurity distributions in the junction region. In principle, diffusion techniques should be able not only to maintain these tolerances but also to produce large-area, low-leakage-current junctions. For this purpose, Westinghouse Electric Corporation emphasized the study of diffused junctions.⁶³

Under contract AF 19(604)-5997, Westinghouse studied the diffusion of acceptor impurities in n-type SiC for the fabrication of a unipolar transistor. Aluminum was chosen as the diffusant. The diffusion techniques and electrical characteristics of aluminum-diffused junctions will be described.

Figure 41 shows the furnace used for these experiments. It is made of a heavy-walled, 6-inch-O.D., 20-inch-long quartz tube. The tube is covered at the ends with two water-cooled brass flanges under pressure, which also serve as electrodes. The heater is a 1-inch-I.D., 24-inch-long graphite tube with two ends tapered and pressed to the brass flanges. Concentric graphite tubes are used as radiation shields.

The hexagonal SiC single crystals used in these experiments were grown by the sublimation process. These crystals are flat hexagonal platelets ranging in size from 2 to 3 millimeters in diameter and from 10 to 30 mils thick. Before diffusion, the crystals are cleaned with HF to remove any silicon oxide that may have formed on the surface. The crystals are placed in alcohol until they are loaded into the furnace.

After diffusion, the crystals are removed from the furnace. Any carbon deposit on the surfaces can be removed by oxidation in air. The same equipment and process can be used for diffusing boron, nitrogen, and other impurities in silicon carbide as well.

c. Grown Junctions⁶⁴

The main advantage of the vapor growth method over fusion and diffusion methods for producing p-n junctions on a silicon carbide platelet is that the impurity distribution of the growth layer can be varied both in area and in the direction of thickness, without being limited by the segregation and diffusion laws. It is possible to prepare multiple p-n junctions with each layer having an almost uncompensated impurity concentration. The success of this method depends largely on controlling the degree of vapor supersaturation and on exposing the true surface of the base crystal for deposition.

The vapor growth experiment was undertaken at atmospheric pressure in the same apparatus as that used for the carrier-gas diffusion studies. The temperature gradient around the crucible was sufficiently high to produce the required degree of supersaturation for growth.

Thin, dark-blue layers of aluminum-doped silicon carbide were grown on colorless n-type silicon carbide platelets. The grown junctions, prepared in a Lely-type furnace at about 2500°C, usually had a colorless transition layer, which was observable even with the naked eye. In contrast, the shallow junction prepared by vapor growth on a pure seed crystal at a lower temperature had no visible transition layers.

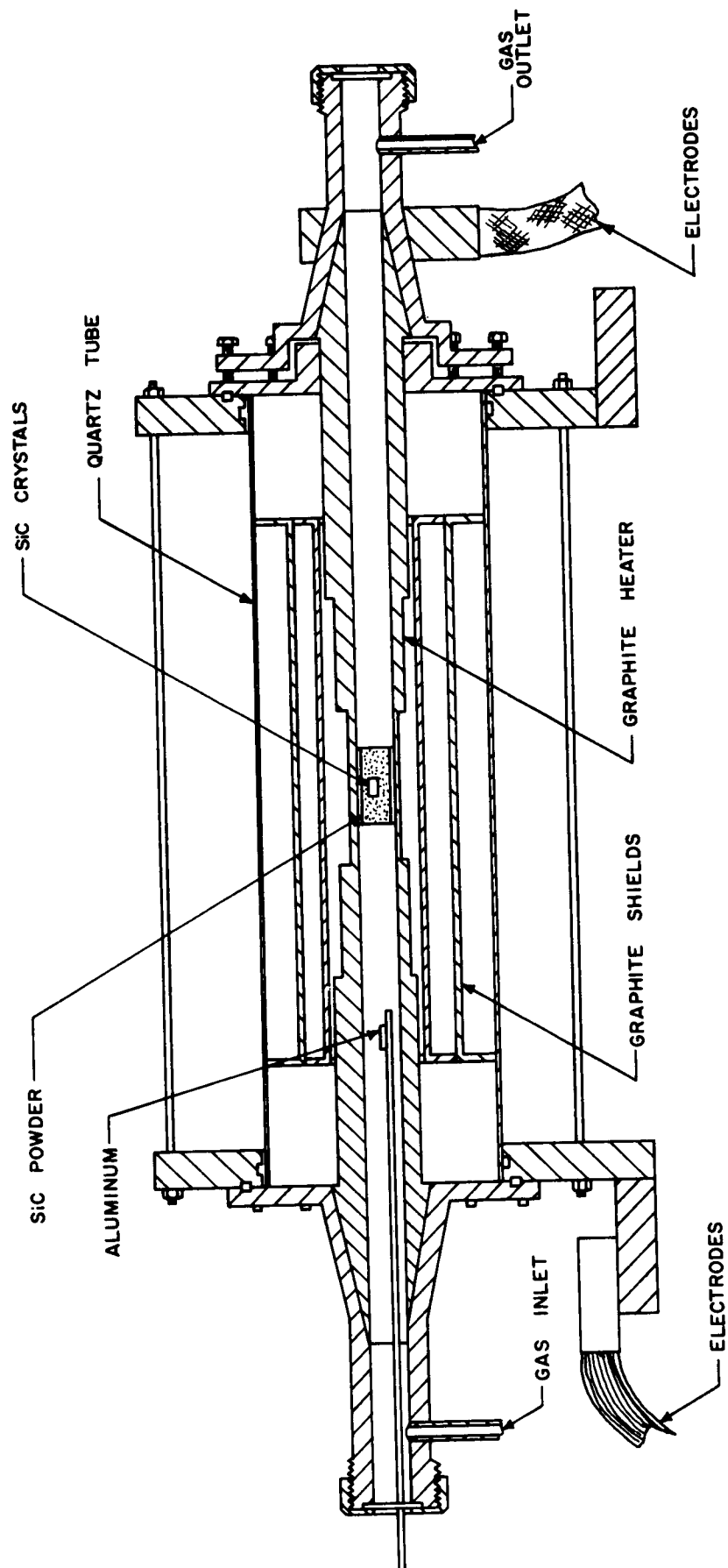


Figure 41. High-Temperature Vacuum-Tight Diffusion Furnace

A uniform growth of single crystal layers occurred, when the platelets were mounted inside the cavity in a favorable position. This position was apparently located so that the surface of the growth layer could dissipate heat uniformly. At very high temperatures, the crystal surface was occasionally covered with carbon aggregates. When this happened, the grown layer was usually polycrystalline. The growth rate was dependent upon the location of the crystal inside the cavity. The average growth rate was of the order of 3 microns per hour.

d. Contacts

A large number of systems have been studied for electrical contacts and solders on silicon carbide, including the elements and alloys used for fusion studies. Westinghouse Electric Corporation⁶⁵ investigated the feasibility of using vacuum evaporation and thin film alloying techniques for the production of ohmic contacts onto silicon carbide devices. The basic idea is to deposit a film of a suitable metal or alloy onto the semiconductor crystal by means of vacuum evaporation. The film is then selectively removed from the surface of the crystal by etching leaving the metal only on the regions where the metallized contact is desired. The remaining metal is subsequently thermally alloyed onto the semiconductor to improve both the mechanical and the electrical properties of the contact.

The deposition of the evaporated metallic films, for the experiments performed by Westinghouse Electric Corporation, was accomplished in a commercial vacuum metallizer which was equipped with an oil diffusion pump and a liquid nitrogen trap. The SiC crystals were lapped and etched in molten Na_2O_2 and then placed onto a graphite strip heater inside a chamber evacuated to a pressure lower than 10^{-5} millimeters of mercury. The graphite was then heated up to about 1100°C for 5 to 10 minutes. After this vacuum baking, the heater was allowed to cool down to about 200°C and at this point the evaporation was performed. The thickness of the film has been, in some cases, monitored during the evaporation by measuring the electrical resistance on the film deposited onto a glass slide. This technique enables evaporation to cease when the desired thickness is obtained. After the evaporation, regions of the metallized SiC surface were masked and the exposed film was removed by etching in a suitable solution.

The alloying was performed by placing the crystals onto a graphite strip heater, which was then heated in vacuum or in a suitable inert atmosphere. In some cases, however, a modified alloying technique was selected, using the arrangement shown in Figure 42. The crystals are placed onto a graphite strip heater, under a molybdenum strip

heater, which can be heated independently. The spacing between the graphite and the molybdenum is about $\frac{1}{8}$ inch. The molybdenum heater is designed to minimize the changes of its position with respect to the graphite due to thermal expansion. In this arrangement, the silicon carbide crystals are preheated by raising the temperature of the graphite heater. During the actual alloying, the samples are heated also by the radiation coming from the molybdenum strip.

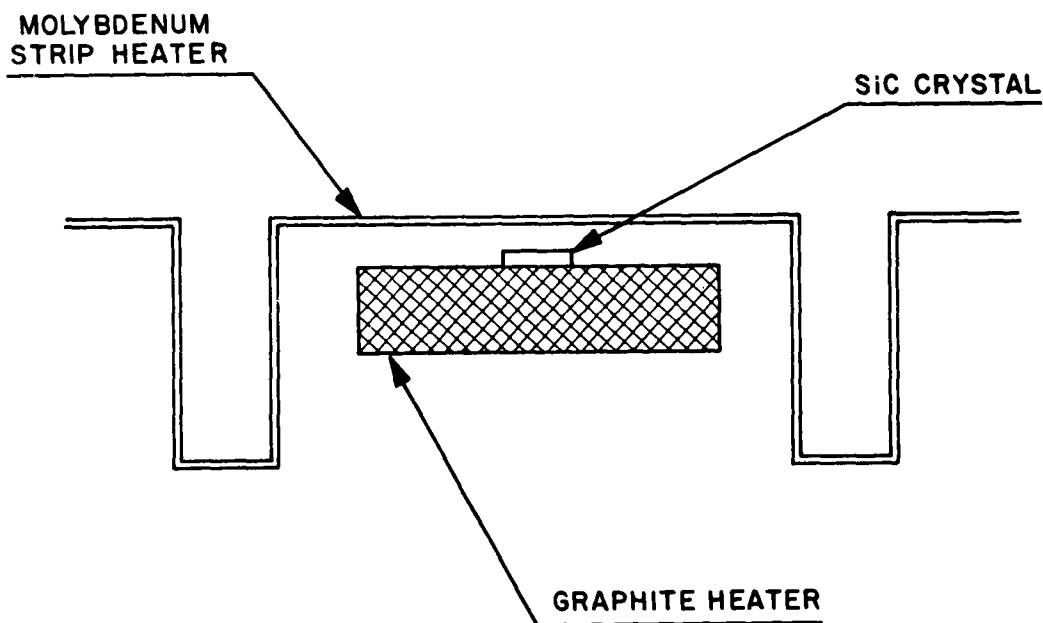


Figure 42. Heater Arrangement for Alloying

Electroless plated contacts to silicon carbide have been reported by Raybold.⁶⁶ The procedure requires very simple equipment and produces a contact having stable electrical and mechanical characteristics and one which may be easily removed, leaving the crystal in its original form. Copper and nickel electroless solutions have been tried. The copper solution gave a good plate, but the solution decomposed soon after mixing and could, therefore, be used only once. Of the different electroless nickel solutions tested, the following solution produced faster and better plating:

| | |
|--|------------|
| Nickel chloride, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ | 30 g/liter |
| Sodium hypophosphite, $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ | 10 g/liter |
| Sodium hydroxyacetate, $\text{NaC}_2\text{H}_3\text{O}_3$ | 50 g/liter |

The crystal may be plated without prior masking, in which case the entire crystal is plated and soldered. The plate and solder are then removed mechanically from the area where they are not wanted. The crystal is then dipped into a mild etch to remove the small traces of solder and nickel remaining on these areas.

2. Mechanical Treatment

Silicon carbide can be cut quite easily with a diamond wheel. Westinghouse Electric Corporation reports cutting of silicon carbide by scribing the surface with a diamond-pointed stencil. The cut side is then placed down on a resilient surface, the edge of a piece of tungsten carbide is placed on top of the silicon carbide over the scribed mark, and the tungsten carbide is struck a sharp blow. The silicon carbide cleaves quite rapidly, and pieces as small as 0.03 inch by 0.06 inch have been cut in this manner.⁶¹

Techniques have been developed which provide precise control of lapping depths. Coupling this control of lapping depths with accurate delineation of the p-n junctions allows one to control the junction depth as well. The general method that has been employed is as follows:

The p-n junction at the edge of the crystal is exposed by lapping or scribing away the edge.

The junction is delineated in a suitable manner.

The amount to be removed is determined.

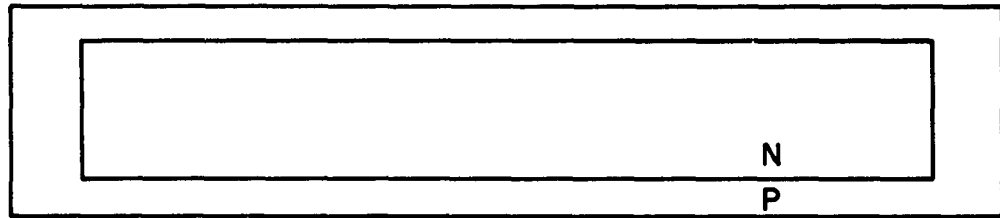
The crystal is mounted on a lapping jig so that it will be lapped parallel to the junctions.

Lapping is performed with coarse abrasive (220 to 320 mesh B₄C) to rough down near the required junction depth and then with finer abrasive (600 to 1000 mesh B₄C) to the final thickness.

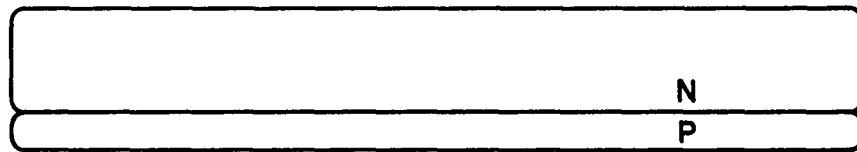
The thickness of the wafer is measured and the position of the surface in relation to the delineated junction is determined.

Using the above method, Westinghouse Electric Corporation obtained depths as shallow as 0.6 mil. Such a lapping technique is being used in a two-step diffusion process for the formation of a unipolar transistor. In this process, the crystal is deeply diffused and the perimeters of the diffusion junctions are exposed and delineated, forming a p-n-p structure. The poorer junction is removed by precise

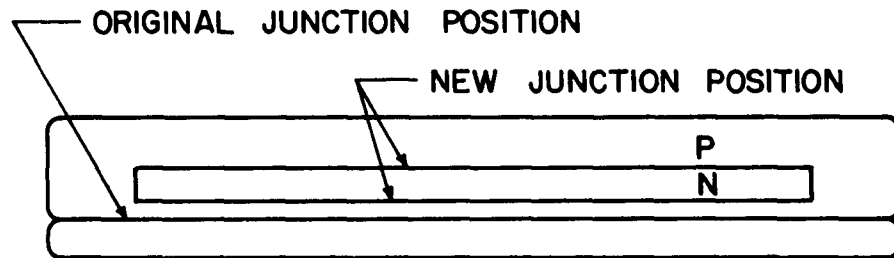
lapping and molten Na_2O_2 etching, giving a p-n structure with a desired thickness of the n-layer. A second diffusion step is used to form a p-region in the thin n-layer, producing again a p-n-p structure with the desired channel thickness. This technique is shown schematically in Figure 43.⁶⁵



A. WAFER AFTER FIRST DIFFUSION



B. WAFER AFTER LAPPING AND ETCHING



C. WAFER AFTER SECOND DIFFUSION

Figure 43. A Two-Step Diffusion Process for the Formation of Device Structures

3. Etching ⁶⁷

When a crystal is cut by abrasive action or abraded by other processes such as lapping, mechanical polishing, etc., the surface is damaged. This damaged layer has a detrimental effect on many fundamental measurements and on device characteristics if it is not removed. Removal of damaged layers is accomplished by etching. The etching process, to be effective, should be controlled, i. e., the etching should have a reproducible rate and be capable of being confined to specified areas. Protection of areas that do not require etching is achieved by masking with a material which is not attacked by the etching agent.

A number of chemical and physical methods can be employed for etching; all that is required is that the process should remove material evenly from the surface and not create a damaged surface. For silicon carbide, chemical or electrolytic etching has been used quite effectively, and these processes will be briefly reviewed.

a. Chemical Etching

Any type of chemical reaction can be used as an etch, provided that the reaction products do not form a layer at the surface. The etch can be a solution, a gas, or a molten salt.

(1) Solutions. In order to etch a material like silicon carbide, it is necessary to form compounds of both silicon and carbon. Silicon is not too difficult to get into solution; hydroxides such as NaOH dissolve silicon to form silicates. However, none of the etches for silicon are potent enough to form compounds with carbon.

Ellis⁶⁸ investigated the etching of silicon carbide with phosphoric acid. His results showed that the reaction of silicon carbide with phosphoric acid at 215°C was too slow and it left a gelatinous silica layer on the surface.

(2) Gases. Reactions with gases can be used for etching of silicon carbide, provided that the reaction products are volatile at the reaction temperature. The action of several gases on SiC has been studied, mainly by investigators in the refractive field. It was found that F₂ readily reacts with SiC, and N₂ reacts at least at 1400°C, forming nitrides of silicon and carbon. However, the silicon nitride remains on the surface, since it is not very volatile, except at high temperatures. There are also numerous possible reactions between SiC and oxygen. Westinghouse Electric Corporation studied oxygen etching of SiC at temperatures ranging from 900° to 1400°C, by weighing the specimens before and after etching.

Since no loss in specimen weight occurred, it was concluded that oxygen etching did not appear to be a promising method for SiC and it was abandoned in favor of more promising methods.

(3) Molten Salts. This appears to be the most promising method for chemical etching of silicon carbide. Table IX⁶⁷ lists several salts that could be used for etching, as well as some salts that give no reaction. For a chemical reaction to be useful for etching, the reaction products should be gaseous or soluble in the etching reagent, as the reactions with halogen and oxygen compounds. The temperature of reaction listed in this table is that temperature which resulted in etching at a reasonable rate.

The chief advantages and disadvantages of chemical etching can be summarized as follows:⁶⁵

Advantages

It is not limited to p-type material like electrolytic etching.

The etch rate is essentially uniform on the surface.

The attacked material is completely removed by the etchant.

Disadvantages

Chemical etchants require high temperatures.

The etchants are extremely corrosive to masking materials.

During molten salt etching, the specimens must be removed from the etchant and cleaned before the extent of etching can be determined.

b. Electrolytic Etching⁶³

Electrolytic etching is an effective method of improving the electrical characteristics after the junction and contacts are made. Selective electrolytic etching plays an important role in revealing and shaping junction structures of silicon carbide. The importance of electrolytic etching as a postetch to the silicon carbide device is greatly increased because of the lack of effective masking techniques for the sodium peroxide etch.

Table IX. Molten Salt Etching of Silicon Carbide

| Salt | Melting Point (°C) | Reaction Temperature (°C) | Remarks |
|---|--------------------|---------------------------|--|
| NaOH | 318 | 900 | approximate etch rate 0.5 milligram per centimeter ² per minute. |
| NaOH | 318 | 500 | no etching after 45 minutes. |
| Borax | 741 | ≥1000 | |
| Cryolite | 1000 | | reaction probably carried out at very high temperature. |
| Na ₂ CO ₃ | 851 | 900 | approximate etch rate 0.1 milligram per centimeter ² per minute. |
| K ₂ CO ₃ | 891 | ~1000 | |
| K ₂ CO ₃ :Na ₂ CO ₃ | - | ~1000 | 3 to 1 ratio. |
| Na ₂ SO ₄ | 884 | | |
| KNO ₃ | 333 | 900 | decomposes at 400°C, no reaction. |
| KNO ₂ | 297 | | decomposes at 350°C, no reaction. |
| NaCl | 800 | 900 | no reaction. |
| KClO ₃ | 368 | | decomposes at 400°C, no reaction. |
| Na ₂ O ₂ | | 500 | decomposes at 460°C, approximate etch rate 0.1 milligram per centimeter ² per minute. |
| Na ₂ O ₂ | | 900 | approximate etch rate 1 milligram per centimeter ² per minute. |
| K ₂ CO ₃ :KNO ₃ | | ~ 900 | 2 to 1 ratio. |

Various electrolytes have been studied by Westinghouse Electric Corporation, including Na_2CO_3 , HClO_4 , $\text{NH}_4\text{-HF}$, $\text{HNO}_3\text{-HF}$, and HF . It has been found that for a comparatively fast etching, a modified solution (CP-4) consisting of 15 cubic centimeters acetic acid, 10 cubic centimeters HNO_3 , 6 cubic centimeters HF , and bromine water was quite satisfactory. The disadvantage of this etch is that the solution attacks the metallic part thereby requiring masking. However, the masking is not needed when platinum alloys are used as contacts.

The platelet containing a p-n junction structure is held by a platinum clip and immersed in the electrolyte. Each prong on the clip is electrically insulated to each other so that a voltage can be applied across the crystal by pressure contact. The crystals are biased so that the section to be etched is positive and no masking is necessary. The etching action occurs very sharply around the periphery of the junction at the p-layer and electrolyte interface while the n-layer remains unetched. Figure 44 shows the structure of the junction periphery after a short etch (A). If the etching is continued, a mesa structure results as shown in (B) of the same figure. The current for this electrolytic process varies from 1 to 10 milliamps for a p-layer ranging in area between 0.005 and 0.03 centimeter².

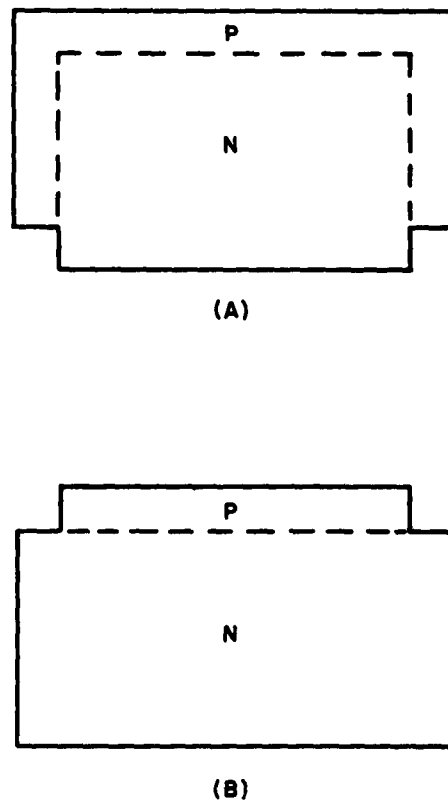


Figure 44. Diffused Crystal Etching

The electrolytic etching technique can be used in removing a selected area of the p-layer for the formation of a device structure. In this case, a separate platinum electrode is used. The p-layer is the anode and the platinum layer is the cathode. The area of the p-layer which is masked with wax will remain unetched.

It would be highly advantageous to be able to etch also n-type silicon carbide electrolytically, so that n-type channel thicknesses in a unipolar transistor of the p⁺n single-gate design could be precisely controlled. In order to do so, holes must be injected in the etching surface by applying a forward bias to the junction, or by illuminating the surface with an ultraviolet light.

The forward bias method is successful only when the n-layer thickness is of the order of the hole diffusion length in n-type SiC, i. e., about 5 to 10 microns (assuming the hole mobility to be 180 to 500 centimeter² per volt-second at room temperature and the hole lifetime to be 10⁻⁸ second). The ultraviolet illumination method has been tried with some success by Westinghouse Electric Corporation in the arrangement shown in Figure 45. The wavelength of the ultraviolet light required was estimated to be from 2000 Å to 3000 Å. A mercury-vapor lamp provided illumination with a continuous spectrum from 2500 Å to 5000 Å. The electrolyte consisted of 2 to 10 percent methyl alcohol solution of 48 percent HF. The rate of dissolution of n-type silicon carbide was very small. After 6 hours of etching at a current density of approximately 2.5 x 10⁻³ ampere per centimeter² only about one micron of material was removed from the surface.

The chief advantages and disadvantages of the electrolytic etching process may be summarized as follows:⁶⁵

Advantages

It is used at room temperature

Masking can be accomplished by common materials.

Disadvantages

It is limited to p-type material unless holes are supplied in some manner to the n-region to be etched.

In most instances, the etched regions are incompletely dissolved, leaving a residue which disturbs further etching.

Advantages

The rate of etching can be varied by varying the current density.

Disadvantages

Rapid lateral attack occurs during etching of broad layers of p-type material on an n-substrate because the current may flow laterally in the p-layer.

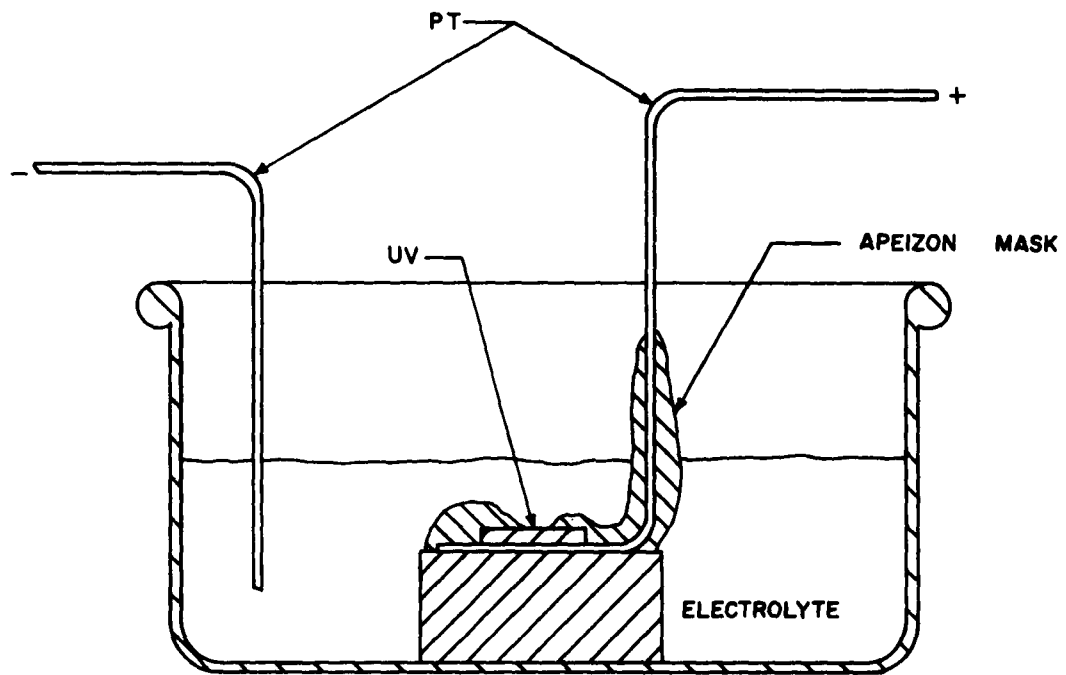


Figure 45. Etching Arrangement for Ultraviolet Illumination

Section V. DEVICES

1. Rectifiers

Rectifiers capable of 500°C operation have been made from silicon carbide crystals containing p-n junctions. These crystals can be grown in a Lely-type furnace. The furnace charge contains elemental aluminum, in addition to the silicon and carbon, so the silicon carbide crystals are p-type at the beginning of the growth period. After a period of crystal growth in this manner, nitrogen is added and the crystals begin to grow with an excess of nitrogen. The crystals are n-type. Figure 46 represents a crystal containing a p-n junction.⁶⁹ The central area is blue and apparently p-type; the outer edge of the crystal is green and n-type.

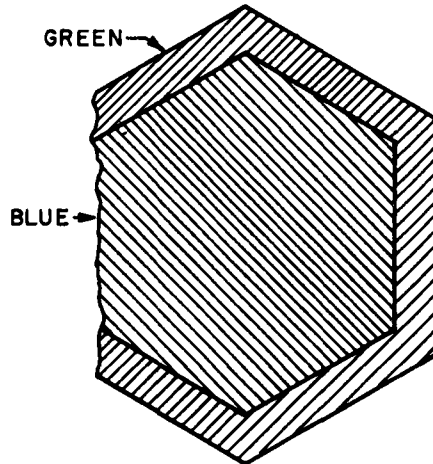


Figure 46. Silicon Carbide Crystal Containing a Grown Junction

The boundary between the blue and green regions is, of course, a rectifying junction. However, the thickness of a crystal such as this is between 5 and 20 mils, so that such a junction would have a small area and be unsuitable as a power rectifier. Although the central area of the crystal is p-type, the top and bottom are n-type. In order to make a rectifying junction from the n-p-n structure shown in Figure 46, it is necessary to remove one of the n-regions and the n-type region at the outer edges, as shown in Figure 47.

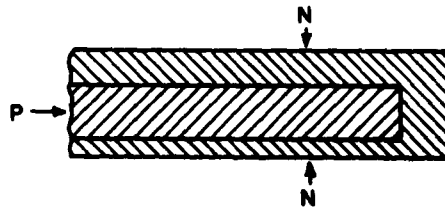


Figure 47. Cross Section of Crystal in Figure 46

The voltage at which breakdown occurs is temperature dependent. A crystal which may be able to sustain a reverse voltage of 200 volts at room temperature may break down at 50 volts at 500°C. This breakdown is usually irreversible. Because of this breakdown effect, it is necessary to test all crystals at high temperatures before encapsulation. If the crystal breaks down, the damaged areas are removed by etching and the crystal is retested. This process of damaging by application of a high reverse voltage at high temperature and then removing the damaged area tends to improve the temperature characteristics. This type of process is continued until no further improvement in reverse characteristics can be obtained.⁷⁰

A high-temperature encapsulation is required to protect the rectifier from mechanical stress and high temperatures. After the contacts are applied to the crystal, the p-type side is fused to a nickel base. At the same time, a nickel-clad copper wire is fused to the n-type side at the top. This fusion is followed by a final electrolytic etch.

Figure 48 shows a cutaway view of the final assembly. The nickel base is welded to a commercial header which is made of a nickel-iron alloy flange, brazed to a ceramic insulating section. A nickel-iron cap, with a stainless steel threaded section, is brazed to the top of the ceramic insulator. A piece of silver rod with a small hole in the center is brazed to the top of the header. The nickel-clad copper wire from the n-side of the rectifier is positioned in this hole.

Characteristics of silicon carbide rectifiers at 500°C are shown in Figures 49, 50, and 51. These measurements were made in completely assembled units. The characteristics were measured in a half-wave rectifying circuit and I_{DC} represents the direct current passing through the load and the rectifier.

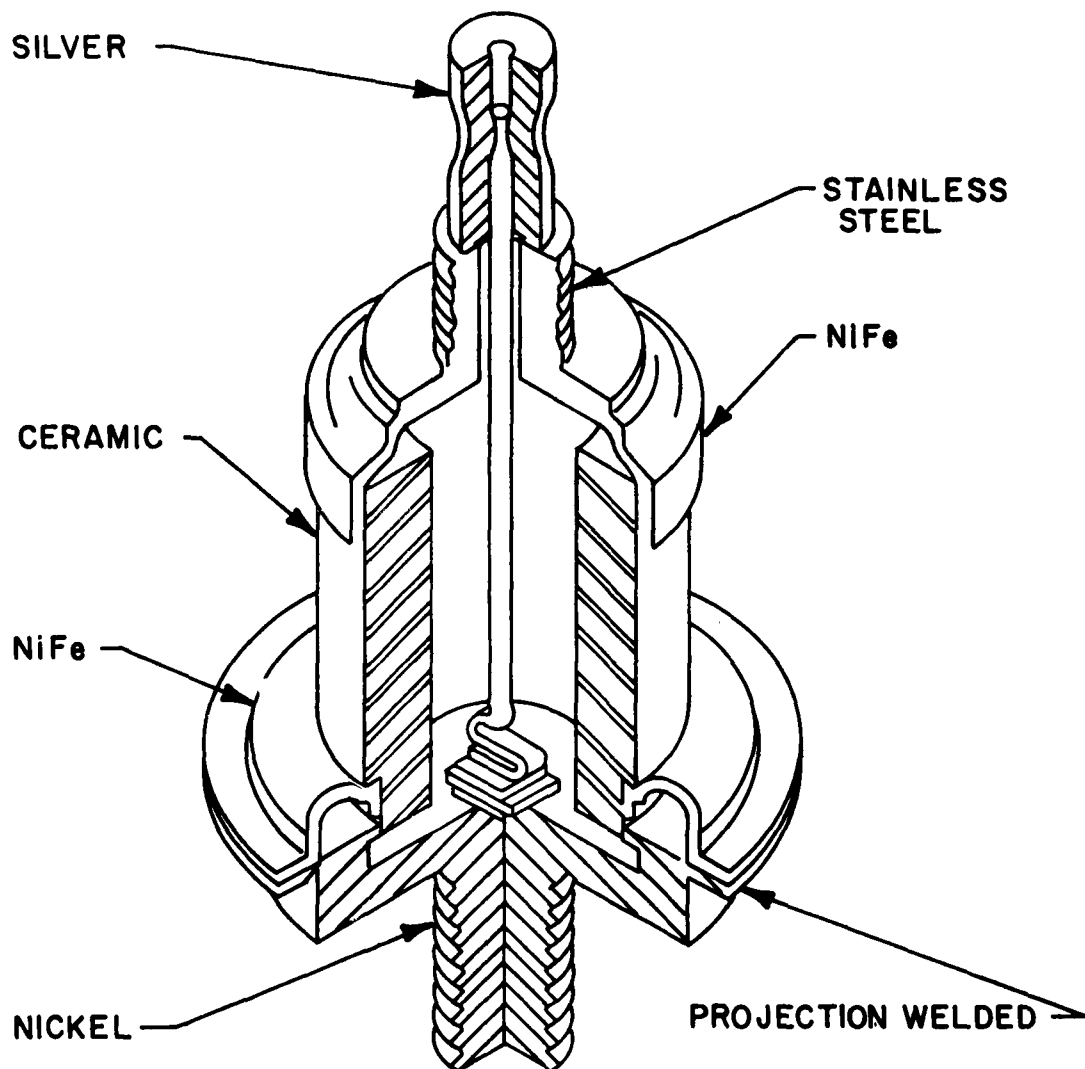


Figure 48. Large Area Rectifier Assembly

Figure 49 shows the forward and reverse characteristics of a silicon carbide rectifier at 500°C, with a peak inverse voltage of 150 volts, with the load resistance adjusted to give dc currents of 0.1, 0.5, and 1.0 ampere. The increase in reverse currents with increased dc current is due to the heating of the junction because of forward voltage drop. Figure 50 shows how the reverse leakage varies with dc current. At the higher dc currents, the heating causes the junction to be at a temperature considerably above the base temperature, and the leakage increases appreciably.

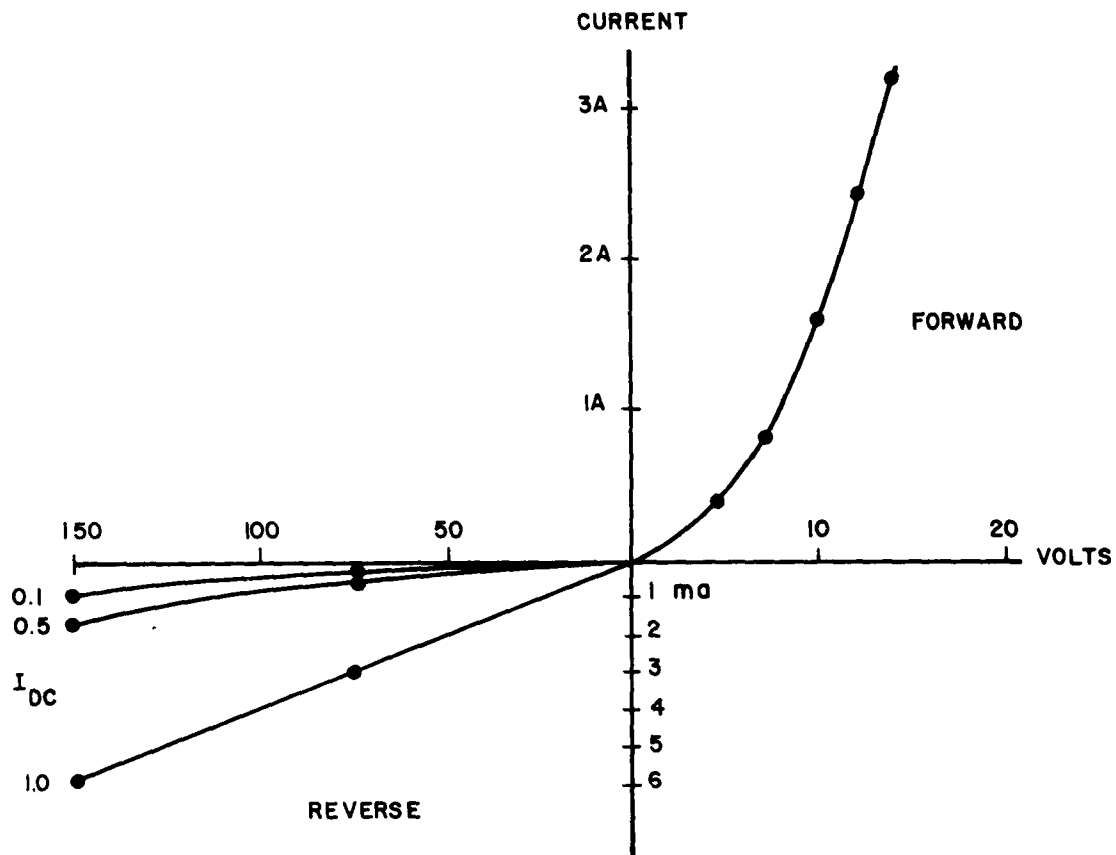


Figure 49. Silicon Carbide Rectifier Characteristics at 500°C

Figure 51 shows the dependence of the rectification ratio upon the dc current being delivered to the load. Rectification ratio is the ratio of the static resistance at the peak inverse voltage to the static resistance at the peak forward current.

Table X shows the rectifier characteristics at temperatures of 100° to 500°C. At temperatures lower than 500°C, the leakage currents are lower but the forward drops are higher.⁶⁹

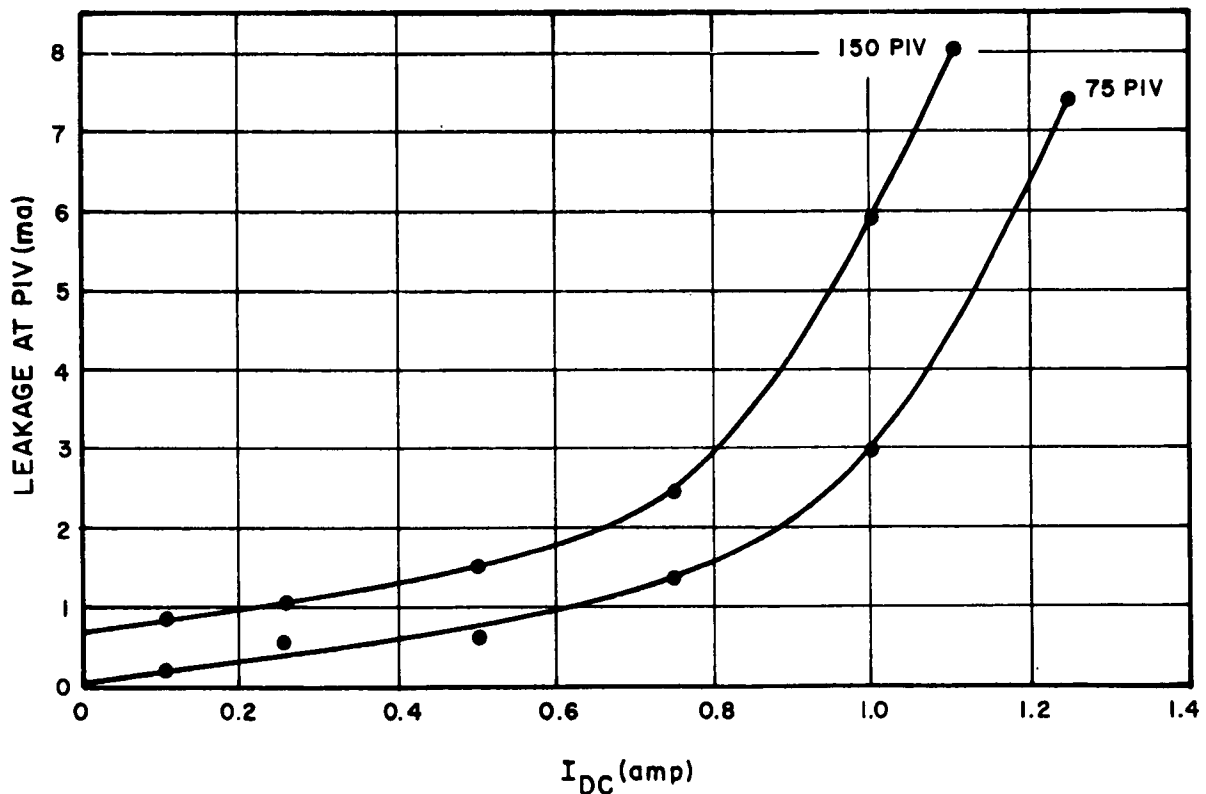


Figure 50. Silicon Carbide Rectifier Characteristics at 500°C

Westinghouse Electric Corporation⁷¹ tested rectifiers under different ambient conditions. One rectifier was tested using water vapor as the ambient. After placing the rectifier into a quartz tube furnace, the system was evacuated to about 10^{-6} millimeter of mercury. The temperature was raised to 500°C and the half-wave average reverse current was 7.3 milliamperes. Water vapor was then introduced into the furnace to a pressure of 25 millimeters of mercury and the reverse current was stabilized at about 50 microamperes at 150 volts. Air was then introduced to the furnace until the total pressure rose to 1 atmosphere, at which time the reverse current remained the same. The system was again evacuated to about 10^{-6} millimeter of mercury, with no change in the reverse current. After cleaning the rectifier with 48 percent HF, dilute HCl, and finally alcohol, the test was repeated, using water vapor, and a mixture of air and water vapor. The reverse current increased very slightly, to 52 microamperes in a vacuum, then decreased again to about 50 microamperes with the addition of water vapor and a mixture of air and water vapor.

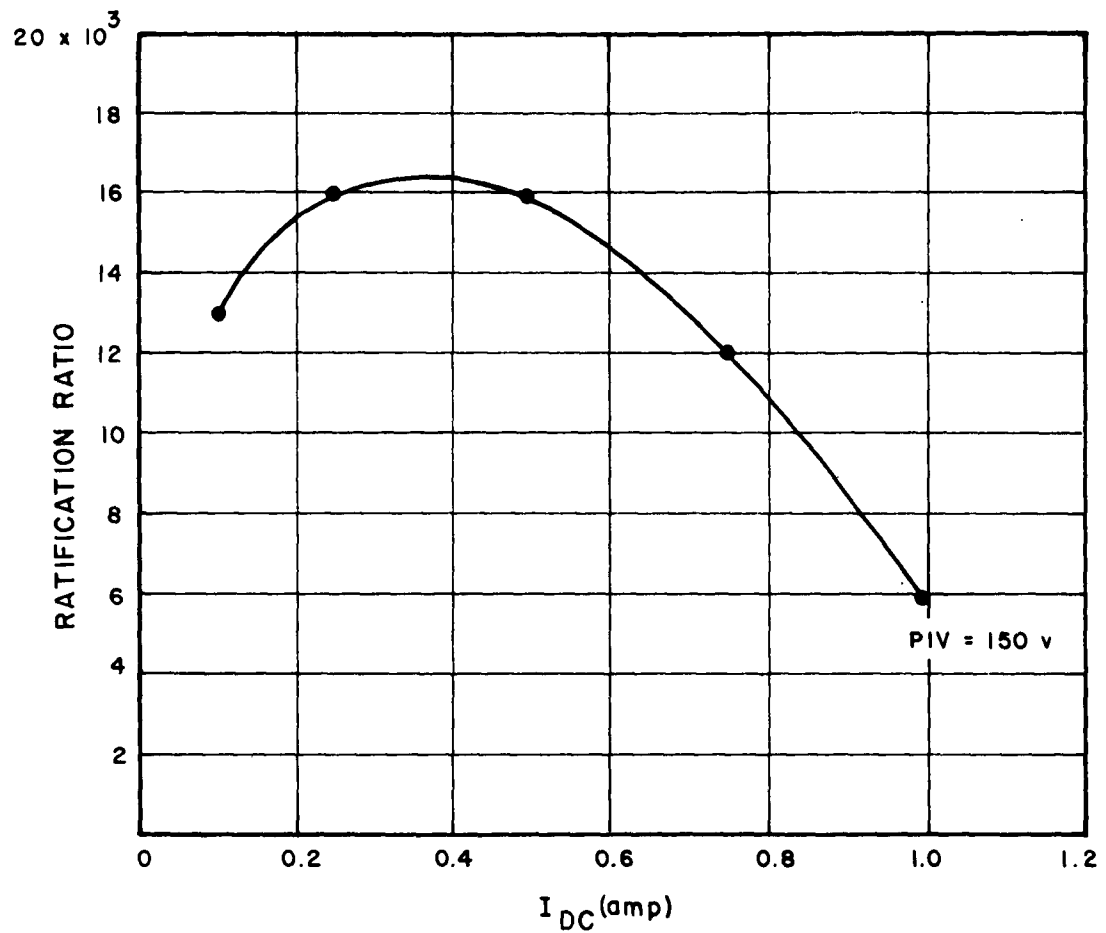


Figure 51. Silicon Carbide Rectifier Characteristics at 500°C

Table X. Effect of Temperature on SiC Rectifier Characteristics

| Temperature (°C) | I_{DC} (A) | Reverse | | Forward | | Rectification Ratio |
|---------------------|-----------------|-------------------|--------------------|-------------------|-------------------|---------------------|
| | | V_{peak} (V) | I_{peak} (ma) | V_{peak} (V) | I_{peak} (A) | |
| 500 | 0.5 | 150 | 20 | 10 | 1.6 | 1200 |
| 400 | 0.5 | 150 | 13 | 12 | 1.6 | 1540 |
| | 1.0 | 150 | 70 | 18 | 3.0 | 358 |
| 300 | 0.5 | 150 | 11 | 13 | 1.6 | 1670 |
| | 1.0 | 150 | 37 | 18 | 3.0 | 645 |
| 200 | 0.5 | 150 | 8 | 16 | 1.6 | 1780 |
| | 1.0 | 150 | 22 | 20 | 3.0 | 1010 |
| 100 | 0.5 | 150 | 4 | 21 | 1.6 | 2520 |
| | 1.0 | 150 | 13 | 23 | 3.0 | 1510 |

Other rectifiers were tested in which only vacuum and helium were used and the temperature varied from 100° to 500°C. The rectifiers were first tested in a vacuum of 10^{-6} millimeter of mercury from 100° to 500°C and then in a pressure of 1 atmosphere of helium from 100° to 500°C. The reduction in reverse current was quite large. At 500°C and a vacuum of 10^{-6} millimeter of mercury, the half-wave average reverse current was 7.0 milliamperes at 150 volts, while in helium the reverse current at 150 volts decreased and remained stable at 80 microamperes. The results of this test are shown in Figure 52.

Figure 53 shows a silicon carbide rectifier through a complete vacuum-helium cycle, from room temperature to 500°C (with the introduction of helium at 500°C) and back to room temperature. When the helium was introduced, the reverse current at 150 volts decreased immediately from 5 milliamperes to about 88 microamperes and remained constant for several hours, after which the room temperature was reduced to ambient.

These experiments served as a further proof that the electrical properties of semiconductor surfaces are affected by small amounts of absorbed monolayer of foreign material. Obviously, further tests are needed to determine what other impurities, in addition to moisture and helium, contribute to the reduction and stabilization of silicon carbide surfaces. Improvements in the processing of rectifiers are continued under contract AF 33(657)-7027.

2. Transistors

The low mobility and short lifetime of silicon carbide, which corresponds to an electron diffusion length of about 3.9 microns, presents technical difficulties in the preparation of a high-temperature transistor. The minimum base width of an n-p-n transistor made of this material would have to be in the order of 2 microns. In order to overcome these difficulties, SiC transistors should be operated on the basis of a field-effect rather than the diffusion of minority carriers. Two basic field-effect devices, the drift and the unipolar transistors, have been investigated by Westinghouse Electric Corporation. The fabrication of a unipolar transistor appears to be more feasible since its operation does not require injection.

N-type α -SiC single crystals with a donor concentration of 10^{14} - 10^{16} cm^{-3} were used for this work. This purity corresponds approximately to a resistivity of 50 to 500 ohm-centimeter at room temperature, depending on the electron mobility and carrier concentration.

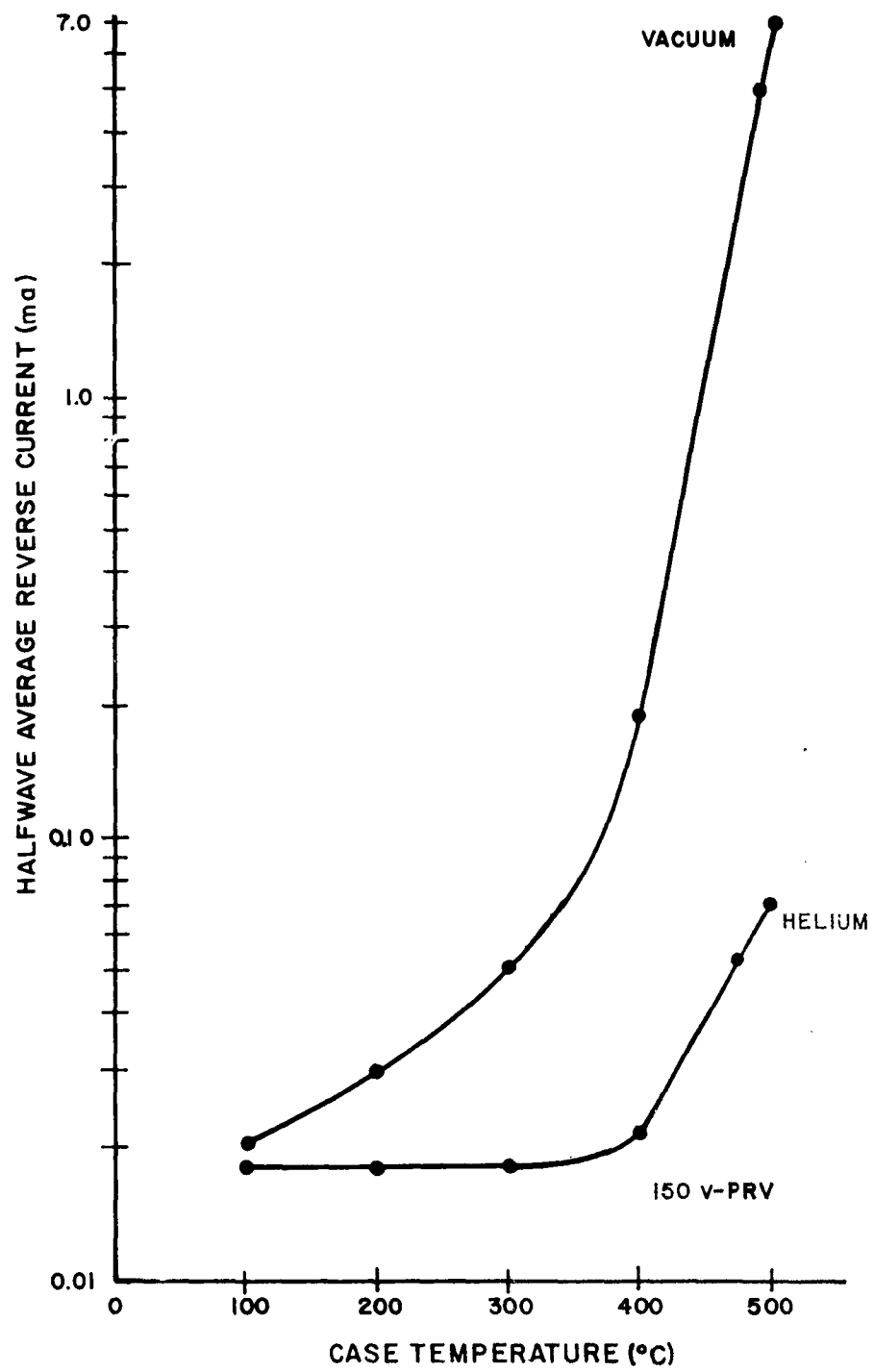


Figure 52. Effect of Impurities on SiC Rectifier Characteristics

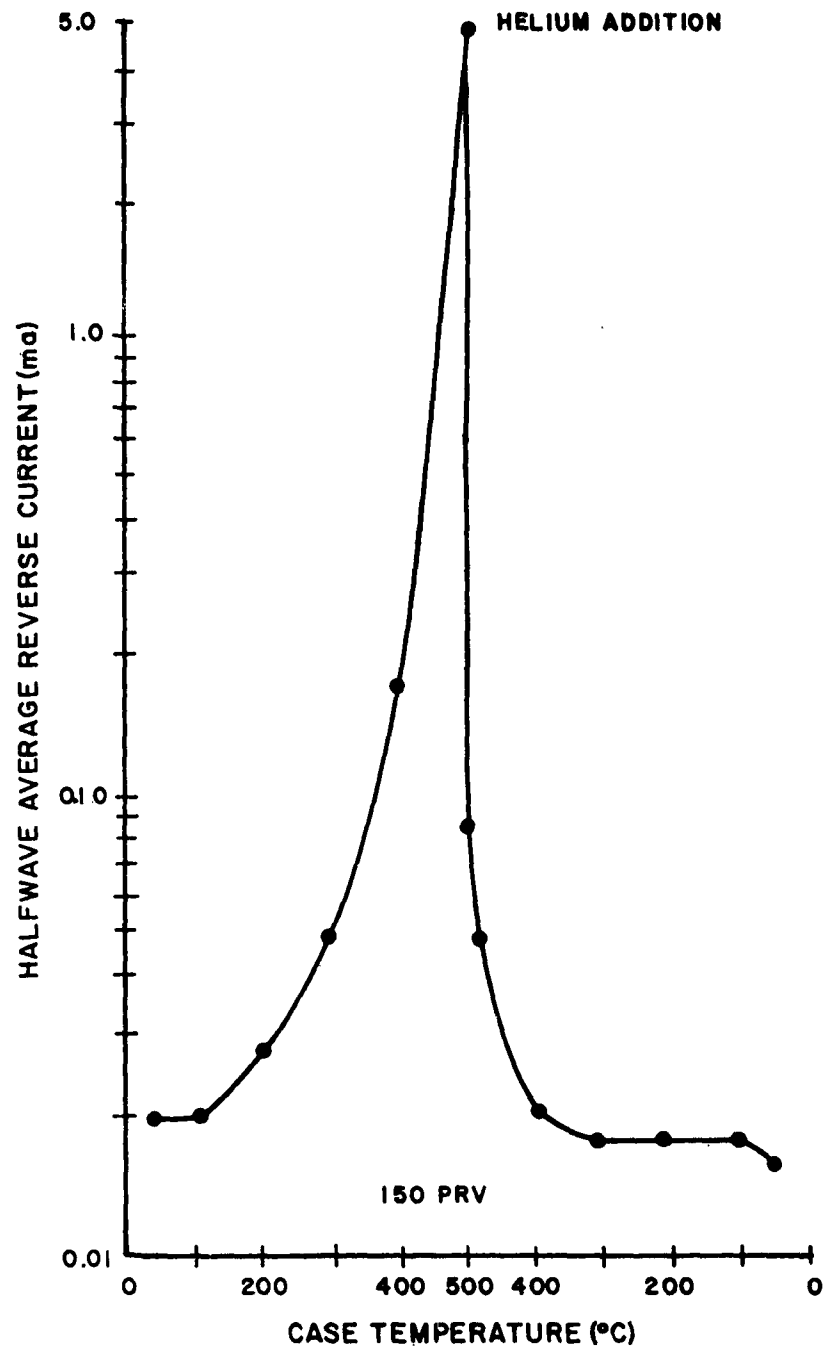


Figure 53. Effect of Impurities on SiC Rectifier Characteristics

The channel thickness, $2a$, is limited by the pinchoff voltage and the purity of SiC, according to the equation:

$$a = (2KW_o/qN)^{\frac{1}{2}}$$

$$\cong 3.35 \times 10^3 (W_o/N)^{\frac{1}{2}}$$

where K is the dielectric constant, q the electron charge, W_o the pinchoff voltage, and N (cm^{-3}) the net ionic impurity concentration in the depletion region. A purity of $N = 10^{14} - 10^{16} \text{ cm}^{-3}$ should give a half-channel thickness, a , in the range of 2 to 20 microns, at which the pinchoff condition can occur at voltages as low as 25 volts.

Another limitation in the design of unipolar transistors is the allowable power dissipation in the unit. This power per unit area of channel, P , can be expressed as

$$P = \frac{2}{3} W_o^2(a/L)^2/ap$$

where L is the length of the channel (centimeter) and p is the resistivity of the channel material. This power dissipation for a SiC device operated at 650°C appears to be in the neighborhood of 1200 watts per centimeter².

Experimental unipolar field-effect transistors, which demonstrate the feasibility of a silicon carbide high-temperature active device, have been fabricated. The fabrication sequence of such a device is shown in Figure 54. The high-purity material had a resistivity of 10 to 100 ohm-centimeters at room temperature. The best results were obtained by diffusing the aluminum vapor into the original surfaces of the crystal. The crystal was then lapped to approximately 3 mils and etched to a thickness of about 2 mils. After diffusion, which produces junction depths of about 20 microns, the p-type diffused skin is removed by electrolytic etching.

The drain characteristics of a unit at room temperature are shown in Figure 55. These measurements were made with 1 K load resistance, which is small in comparison to the channel resistance. Drain characteristics of this same unit, with $V_g = 0$ as a function of temperature, are shown in Figure 56. The load resistance for these measurements was matched with the channel resistance, resulting in a change of drain characteristics. It is apparent from these curves that device characteristics of transistors are strongly dependent upon temperature. The static transconductance of the unit changes from 190 micromhos at 26°C to 13 micromhos at 500°C , for a 2-volt bias. This unit gave an ac power gain of 380 at 26°C , and 7 at 500°C .

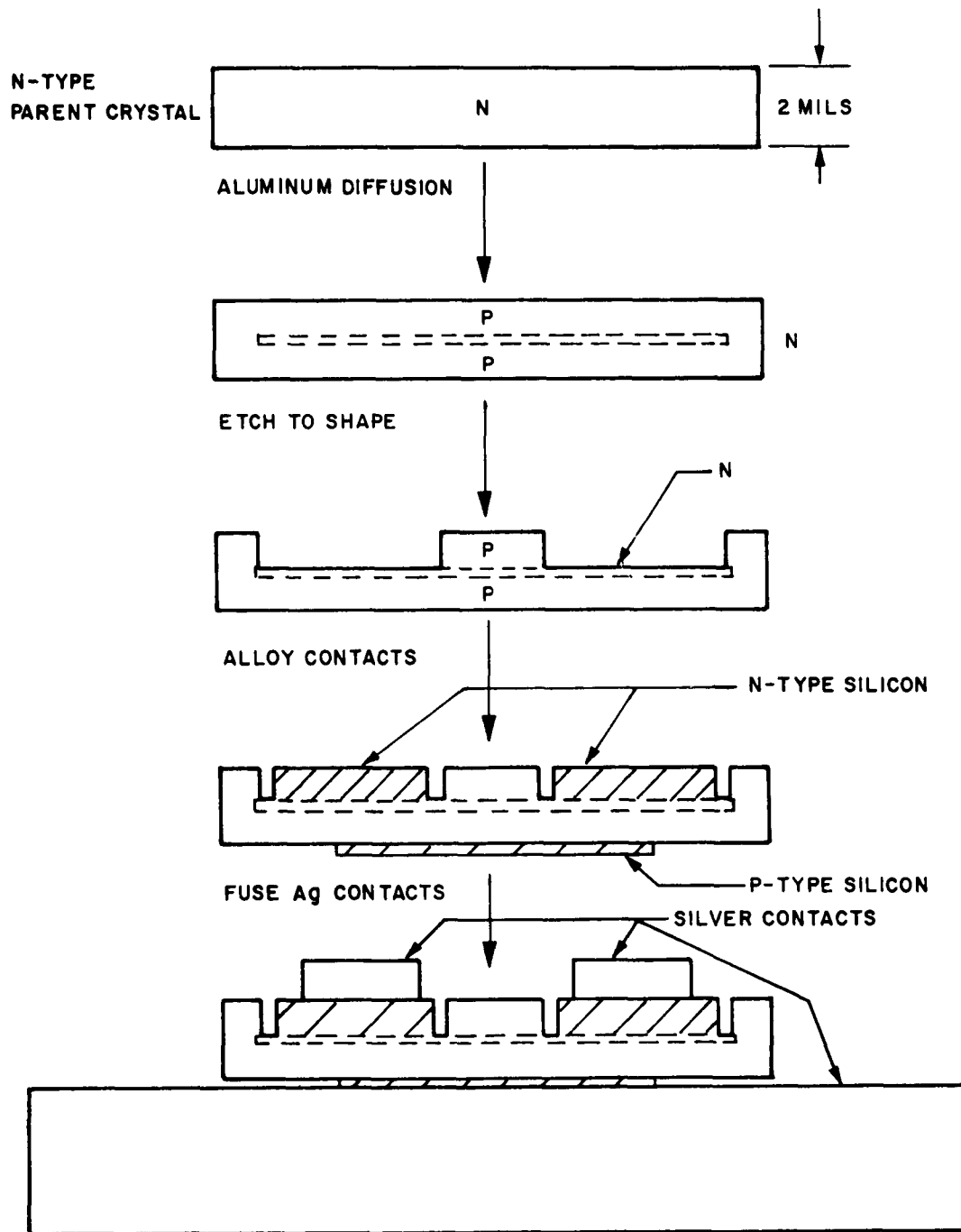


Figure 54. Schematic of Fabrication Sequence for a Double-Gate Diffused Junction Transistor

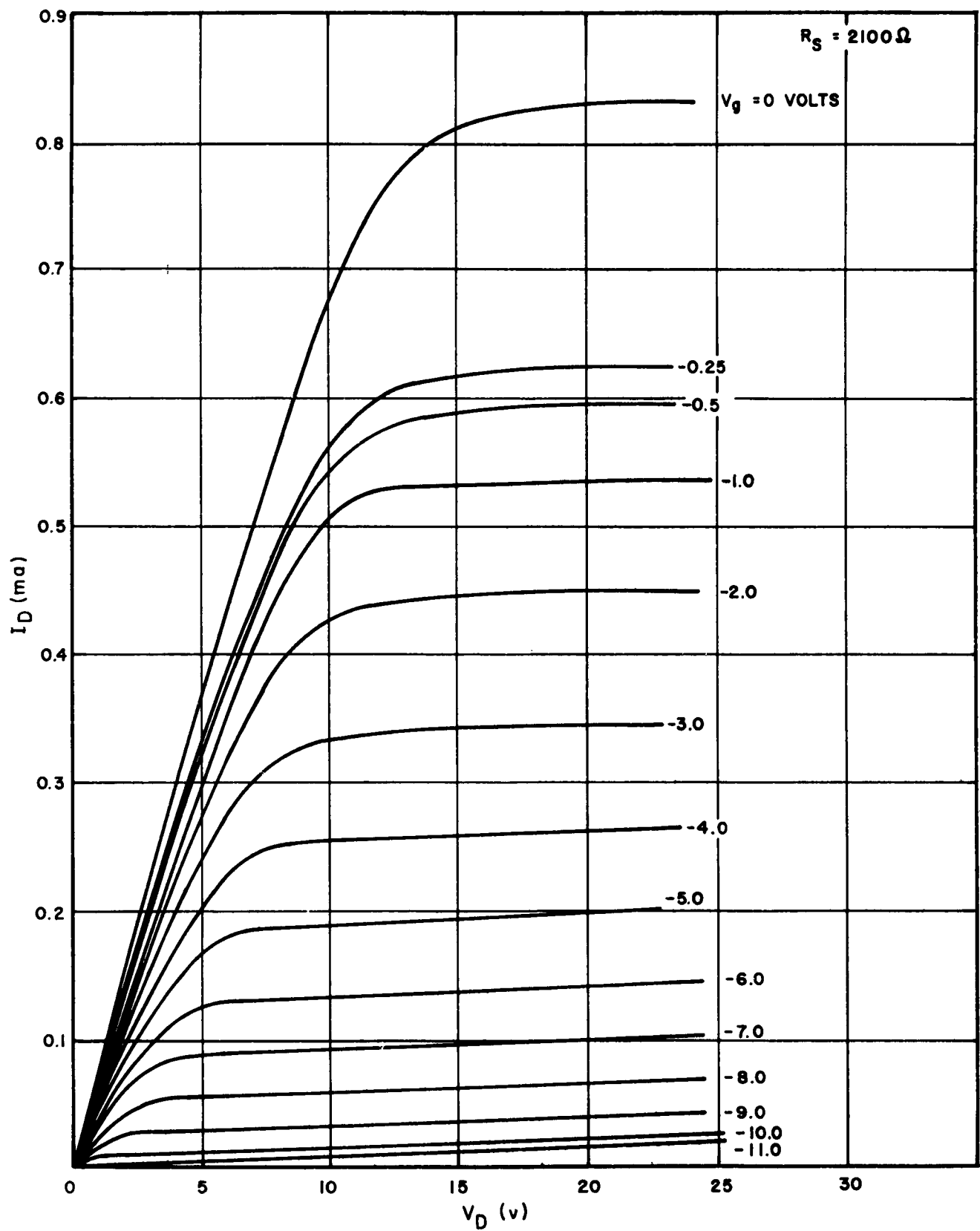


Figure 55. Drain Characteristics

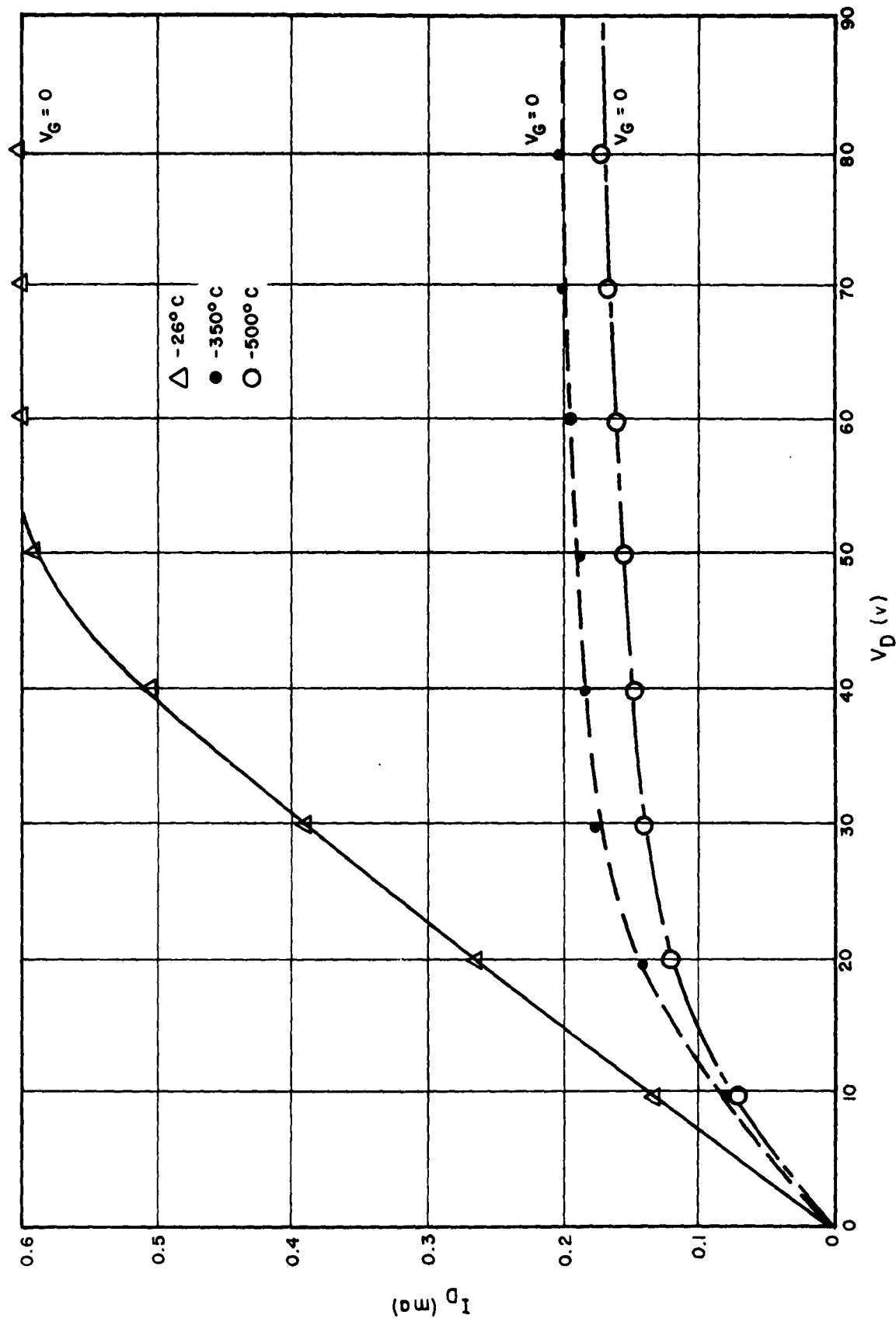


Figure 56. Drain Characteristics Versus Temperature

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A method is described for the analysis of nickel, manganese, copper, zinc, antimony, molybdenum, and iron in silicon carbide. The inherent sensitivity of the method ranges from 0.01 parts per million for iron to less than 0.001 parts per million for manganese. The impurities in the silicon carbide are activated by neutrons in a nuclear reactor. The activated impurities are removed from the silicon carbide by decomposition of the matrix. The impurities are caught in a trap and separated by the radiochemical procedures described herein. Results obtained are given.

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The dislocation structure of type 6H hexagonal silicon carbide has been studied by etching combined with optical microscopy and by X-ray diffraction microscopy. The validity of the conventional etching technique for identification of the sites of the intersection of dislocations with (0001) surfaces has been established. However, high densities of dislocations lying in (0001) planes and hence heretofore undetected by etching techniques were often observed by diffraction microscopy. Dislocations with $[1120]$ vectors have now been found with evidence for slip both on basal planes and on a puckered pyramidal plane. Pileups formed by slip and dislocation walls formed by climb were also observed. Silicon carbide shows many of the characteristics of more conventional plastically deformable materials.

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THE ANALYSIS OF SILICON CARBIDE. Zeitschrift Fuer Chemie. Leipzig, Vol. 3, No. 2, pp. 70-72. 1963. (In German).

Full experimental details are given for the polarographic and oscillopolarographic determination of Cu and Fe_2O_3 simultaneously

in silicon carbide. The oscillopolarographic method is slightly less accurate than the polarographic method, but results from both procedures compare satisfactorily with those of the usual electrogravimetric method.

4. Army Electronic Research and Development Agency, Fort Monmouth, New Jersey.
A TWINNING STUDY OF CUBIC (BETA) SILICON CARBIDE.
Kohn, J. A. and Eckart, D. W. 19 March 1962. (AD-403544).

A study of 25 pure and doped beta SiC crystals by the Weissenberg X-ray method showed prolific twinning (normal and high-order), some stacking randomness, and one case of polytypism (15R). Only two crystals were structurally pure. No clear correlation between these findings and morphology or doping could be established. High-order twinning in beta SiC is discussed, with emphasis on the relationship of a multiple-individual, nonparallel, twin complex to its resultant Weissenberg diffractometry.

5. Aukerman, L. W.
RADIATION-PRODUCED ENERGY LEVELS IN COMPOUND SEMICONDUCTORS. Journal of Applied Physics, Vol. 30, No. 8, pp. 1239-1243. August 1959.

The effects of high-energy radiation on the electrical properties of compound semiconductors are reviewed. Emphasis is placed on those effects which can be interpreted in terms of energy levels. The following compounds are discussed: InSb, InAs, GaSb, AlSb, GaAs, InP, CdTe, and SiC. The implications of bombardment-produced changes in carrier concentration on possible energy levels are considered. Of the compound semiconductors, only InSb, irradiated at 200°K with electrons, has been sufficiently studied to enable a determination of the positions of the energy levels and their rates of generation. The annealing behavior of both InSb and GaSb is complex. A possible interpretation of these annealing characteristics, in terms of shifting energy levels, is discussed.

6. Azuma, K., Ohta, K., and Tomita, T.
THE CRYSTAL STRUCTURE OF SiC 39H. Journal of Physical Society of Japan, Vol. 18, pp. 1097-1098(L). July 1963.

7. Bell Telephone Laboratories, Inc., Whippany, New Jersey.
NEEP. NUCLEAR ELECTRONIC EFFECTS PROGRAM.
Final Report. 1 March 1959 - 31 October 1962. ASD TDR 63-127. (AD-403432). Contract AF 33(616)-6235.

The effects of nuclear radiation on semiconductor materials and devices are presented. Electron and neutron damage in germanium and silicon was studied to determine the nature of the interactions and damage centers and their effects on the properties of these materials. The effects of space radiation and radiation from the Van Allen Belts on solar cells and satellite electronic components were evaluated. A selected spectrum of semiconductor devices was studied to determine the permanent radiation damage to these devices and the effects on their electrical parameters. These results were then employed in evaluating the degradation of circuits incorporating these devices.

8. Bennett, A. I. and Longini, R. L.
DENDRITIC GROWTH OF GERMANIUM CRYSTALS. Physical Review, Vol. 116, No. 1, pp. 53-61. 1 October 1959.

Controlled dendritic growth of germanium from the melt yields long thin strips whose principal surfaces are optically flat $\{111\}$ crystallographic planes except for the occasional presence of small steps. The crystals grow rapidly in the $\langle 211 \rangle$ direction, have twin planes parallel to the flat surfaces, and can withstand an elastic strain exceeding 10^{-3} . The distribution coefficients of impurities are close to unity compared to quasi-equilibrium values. A mechanism for dendritic growth is proposed, in which the presence of at least one properly oriented twin plane is fundamental and necessary. This mechanism explains most of the observed growth features in germanium dendrites, and is expected to apply generally to materials with the zincblende structure. The presence of the twin plane makes growth in opposite directions in the twin plane dissimilar (not only in the zincblende lattice, but generally). The effect of the asymmetrization on the growth of α -SiC is considered. A proposed crystal growth mechanism, based on the asymmetrization, should be of general validity.

9. Bhide, V. G.
SPIRAL PITS ON SILICON CARBIDE. Nature, London, Vol. 181, pp. 1006-1007. 5 April 1958.

Terraced pits were observed on silicon carbide crystals, with step heights of $27 \pm 2 \text{ \AA}$ and 1050 \AA . The structure of the pits indicates that evaporation takes place in accordance with a dislocation mechanism.

10. Bohm, J.
THE GROWING OF SILICON CARBIDE CRYSTALS WITH SPECIAL CONSIDERATION OF PURITY. Reinststoff Wiss. Tech., International Symposium, 1, Dresden 1961, pp. 337-344. 1963.

SiC crystals were grown in the apparatus described before (Neue Huette 6, 638-43(1961)) and were examined for their impurity content. The crystals were comminuted in a diamond mortar by 2 steel hammers, so that spectral analyses could be performed on all impurities except Fe, Mn, and Cu, the results of which were affected by the comminution treatment; these 3 were analyzed by radioactivation in a nuclear reactor followed by chemical decomposition in a Cl + O stream at red heat. The reference for the spectral analysis was semiconductor-pure Si, which was transformed into SiC when ignited between graphite electrodes. The impurity contents in percent weight of the technical SiC (green, fine-grained, and prepurified) and of the SiC crystals grown were, respectively: Ca 1×10^{-3} and 5×10^{-4} ; Mg 3×10^{-3} and $5 \times 10^{-5} - 3 \times 10^{-4}$; Al 5×10^{-3} and 3×10^{-3} ; Ti 1×10^{-2} and 1×10^{-2} ; V 3×10^{-3} and $5 \times 10^{-4} - 3 \times 10^{-3}$; Fe 5×10^{-2} and $5 \times 10^{-4} - 5 \times 10^{-3}$; Cr 1×10^{-3} and $1 \times 10^{-3} - 5 \times 10^{-3}$; Ni 1×10^{-3} and $1 \times 10^{-4} - 1 \times 10^{-3}$; Cu 1×10^{-4} and 1×10^{-7} , and P 1.5×10^{-4} and 3×10^{-5} . Since the contents of only some of the impurities decreased appreciably, purer raw material must be used in this process. Since Si and graphite can be prepared in very pure states, preliminary experiments were done to check the possibility of using them as raw material in the same apparatus for growing very pure SiC crystals. It was observed that various hot points in the furnace, especially the soot layer with its high adsorption capacity, served as impurity sources, hence very pure graphite should be used in furnace construction. Having developed a method for series treatment of X-ray diffraction rotating-crystal photographs, the SiC crystals prepared were analyzed by rotation around the c axis. Despite variations in the crystal growth parameters over considerable ranges, almost all crystals were of the 6H type, and rarely were 4H and 15R type crystals found. Crystal material deposited on cold places in the apparatus were of the cubic type. A unidimensional

defect-ordering of the layers in the direction of the c axis was observed in almost all photographs to a greater or lesser degree, and was frequently associated with diverse structural types. Etching with alkali carbonates, borates, or peroxides showed the presence of small etching cavities, which indicated dislocations pushing through the base plane at sufficiently large angles. Arrangements of such cavities in series indicated plastic processes which have occurred at high temperatures only, in the hard SiC.

11. Bradshaw, S. E. and Mlavsky, A. I.
THE EVAPORATION OF IMPURITIES FROM SILICON.
Journal of Electronics, Vol. 2, No. 2, pp. 134-144. September 1956.

It is shown that the concentration of impurity in a silicon crystal grown in a vacuum is governed by the rate of evaporation and the growth conditions. Three cases of practical interest are distinguished: (1) When evaporation of volatile impurities from the melt is substantially complete before growth of the crystal is begun, boron and aluminum are the only residual impurities from groups III and V. (2) An added impurity, such as phosphorus, is distributed uniformly in a crystal when the growth time, from the moment of addition, has a critical value. (3) Repeated addition of an impurity, such as antimony, to a melt containing an impurity of opposite type, produces a series of identical p-n junctions in the growing crystal, the type of junction produced being controlled by the growth conditions employed. Equations describing the combined effects of evaporation and segregation are derived, and the rates of evaporation of certain impurities are calculated.

12. Brander, R. W.
EPITAXIAL GROWTH OF SILICON CARBIDE. Journal of Electrochemical Society, Vol. 111, No. 7, pp. 881-883. 1964.

Good epitaxial SiC crystals were grown at temperatures up to 2700° and in a pressure range of 0.1-100 μ at rates of 0.5 μ /min, provided the vapor stream did not impinge on the growing crystal surface. X-ray examination showed that layers grown > 1900° were perfect polytype reproductions of the substrate. At lower temperatures, different polytypism occurs, and at sufficiently low temperatures cubic crystals may nucleate.

13. British Ministry of Aviation, Royal Aircraft Establishment, Farnborough, Hants, England.
PREPARATION OF SINGLE CRYSTALS OF SILICON CARBIDE AND CONTROL OF THE FORM AND AMOUNT OF INCLUDED IMPURITIES. Lely, J. A. March 1960. Report No. B/MOA RAE Lib Trans 885.

Hexagonal single crystals of SiC were prepared by sublimation of commercial, bright green SiC at 2500° to 2600°C. The resulting crystals are colorless. Inclusion of elements of group 3 in the lattice produced crystals which were blue and showed defective conductivity. Elements of group 5 produced a green color and excess conductivity.

14. Brown University, Providence, Rhode Island.
RESEARCH DIRECTED TOWARD THE INVESTIGATION OF SILICON AND SILICON-CARBIDE SURFACES. Dillon, J. A., Jr. January 1959. Scientific Report No. 1, 1 October - 31 December 1958. AFCRC TN 59-112. (AD-208866). Contract AF 19(604)-4568.

A review of some of the previous work on the thermal etching of metal and semiconductor single crystals is given, and new data concerning the role of the ambient pressure in thermal etching are presented. The results for silicon indicate that (1) At temperatures exceeding 1000°C where evaporation of the silicon becomes important, thermal etching occurs even under high-vacuum ($1 < 10^{-9}$ mm Hg) conditions. Silicon can be heated at lower temperatures for many hours in high vacuum without evidence of thermal etching. (2) At higher ambient pressures, of the order of 10^{-5} mm Hg, thermal etching takes place at temperatures as low as 800°C. This is apparently due to the formation of volatile surface compounds. The effects of ion bombardment on semiconductor surfaces are discussed, and results for prolonged bombardment of the (100) face of a germanium single crystal are presented. The latter indicate that if argon-ion bombardment, under the conditions used for surface cleaning, is continued for a period about 4 times the cumulative bombardment used in the cleaning experiments, electron-microscope photographs show the presence of etch pits on the surface. These pits have dimensions of the order of tenths of a micron and cover less than 5 percent of the surface. Bombardment experiments at higher current densities are in progress.

15. Brown University, Providence, Rhode Island.
RESEARCH DIRECTED TOWARD THE INVESTIGATION OF
SILICON AND SILICON-CARBIDE SURFACES. Dillon, J. A.,
Jr. and Oman, R. M. Scientific Report No. 2, 1 January -
31 March 1959. AFCRC TN 59-172. (AD-214411). Contract
AF 19(604)-4568.

A review is made of studies of the interaction of O with silicon-carbide surfaces and the resultant effects on electrical properties. Surfaces cleaned in ultrahigh vacuum by Ar-ion bombardment and 1000°C heating absorbed O at room temperature with a sticking coefficient of the order of 0.01. The adsorption increased the work function by about 0.40 electron volt and decreased the photoelectric yield to about one-third the clean-surface value. Differences in O adsorption on different crystal faces were observed which were possibly associated with asymmetry in atomic species on these faces. Oxidation studies conducted at temperatures above 900°C and at pressures of about 1 atmosphere indicated the formation of an SiO₂ layer at the surface. After prolonged Ar-ion bombardment at current densities of about 1 milliampere per square centimeter and at an energy of 500 electron volts, etch patterns visible with an optical microscope appeared on the surfaces of Ge and Si. The patterns were circular, oval, and a distorted circular shape on the (111), (110), and (100) faces, respectively. The development of these faces was not influenced by the outgassing history of the samples or whether the gas employed was Ar, O, or a mixture of the two.

16. Brown University, Providence, Rhode Island.
RESEARCH DIRECTED TOWARD THE INVESTIGATION OF
SILICON AND SILICON-CARBIDE SURFACES. Dillon, J. A.,
Jr. and Oman, R. M. July 1959. Scientific Report No. 3,
1 April - 30 June 1959. AFCRC TN 59-384. (AD-225651).
Contract AF 19(604)-4568.

Investigation of the properties of SiC surfaces following chemical treatments have been undertaken. When the samples are etched in sodium peroxide at about 400°C, one side of the crystal becomes frosted while the opposite side is quite smooth, with a number of hexagonal etch pits visible under examination with an optical microscope. This difference in etching is presumably due to the asymmetry in atomic species on opposite faces. There appeared to be no correlation between this etching behavior and such gross surface properties as defect density

and stepped structure. For n-type samples, there was a correlation between the etching behavior and the oxygen adsorption mode previously studied for sides which had the higher rate of adsorption (possibly the silicon sides) were those which had the smoother appearance after etching. For the one p-type sample whose adsorption behavior was known, the etching behavior was just the reverse. Local irregularities in the distribution of impurities result in differences in type and rectification behavior from point to point on the surface of natural crystals. Further information has been obtained concerning the condition of germanium surfaces following chemical etching. The electron microscope photographs show patterns of a completely different nature than those obtained after ion bombardment. This lends credence to the belief that the pattern previously observed represented the initial steps of ion-bombardment etching.

17. Brown University, Providence, Rhode Island.
RESEARCH DIRECTED TOWARD THE INVESTIGATION OF
SILICON AND SILICON-CARBIDE SURFACES. Dillon, J. A.,
Jr. and Oman, R. M. Final Scientific Report, 1 October 1958 -
30 September 1959. AFCRC TR 59-199. (AD-228984).
Contract AF 19(604)-4568.

The contents of this document are given below.

Ion-bombardment etching of silicon and germanium

Low-pressure experiments

High-pressure experiments

Thermal etching of silicon crystals

Experimental arrangement

Results of heating at intermediate pressure

The interaction of oxygen with silicon-carbide crystals

High-vacuum experiments

High-pressure experiments

Intermediate-pressure experiments

Silicon-carbide surfaces

Gross surface properties of natural crystals

Asymmetry in atomic species

Chemical etching

Point-contact rectification measurements

Correlation of etching behavior with adsorption rate.

18. Brown University, Providence, Rhode Island.
INVESTIGATIONS OF SURFACE PROPERTIES OF SILICON
AND OTHER SEMICONDUCTORS. November 1962. Final
Report, 1 October 1959 - 30 September 1962. AFCRL 62-949.
(AD-295624). Contract AF 19(604)-5986.

Information is given on intermetallic compounds, germanium fast surface states, structure of a cleaved germanium surface, silicon-carbide surfaces, asymmetries in compound semiconductors, and atomically-clean surfaces.

19. Brownell, Wayne E.
CERAMIC MATERIALS. Machine Design, Vol. 35, No. 15.
1963.

Brownell discusses the expanded range of applications and gives the strength, thermal properties, electrical resistivity, and dielectric constants of a number of materials in tabular form. Other properties are also covered briefly, together with some of the production processes. Included are glasses, porcelains, Al_2O_3 , B_4C , SiC , and titanates.

20. Bryson, Vern Elrick.
ANNEALING OF RADIATION DAMAGE IN SEMICONDUCTING
DEVICES. Master's Thesis at the Air Force Institute of
Technology, Wright-Patterson Air Force Base, Ohio. Report
No. GNE-2. March 1959.

This thesis concerns the results and discussion of experiments to determine the effects of radiation upon silicon carbide diodes. An apparently previously unreported electrical field sweeping effect was discovered and studied. This effect occurred when a voltage was applied to the diode in either forward or back direction. This applied voltage appears to remove all accumulation of radiation effects of a permanent nature to the extent that a constant back current characteristic could be maintained during irradiation from 0 to 1.18×10^{16} nvt. After 1.18×10^{16} nvt integrated dose, the diodes tested had a forward to back current ratio of approximately 7400, indicating these devices to be as good as they were at the beginning of the experiment.

21. Canepa, P. C., Malinaric, P., Campbell, R. B., and Ostroski, J.
HIGH TEMPERATURE NUCLEAR PARTICLE DETECTOR.
Scintillation and Semiconductor Counter Symposium, 9th,
Washington, D. C., 26-28 February 1964. IEEE Transactions
on Nuclear Science, Vol. NS-11, pp. 262-270. June 1964.

This report gives AEC-Euratom-supported research. Description of a nuclear particle detector developed from silicon carbide which can detect charged particles and, with the addition of a fissionable coating, thermal neutrons at temperatures in excess of 700°C. For these detectors, n-type SiC crystals grown by the sublimation technique and doped with nitrogen were used. The electrical and counting characteristics of these detectors are investigated, and it is found that the most pertinent properties involved are the purity and perfection of the initial crystal and the junction depth and depletion region of the diode. Studies in which selected diodes were irradiated with electron and proton beams, with alternate irradiation and annealing, are discussed. The studies indicate that these diodes are far more resistant to radiation damage than the best silicon detectors, and should be useful for specialized applications in reactor cores and the casings of nuclear engines.

22. Carborundum Co., Niagara Falls, New York.
A STUDY OF FUNDAMENTAL MECHANICAL PROPERTIES OF CERAMIC SINGLE CRYSTALS. Batha, H. Dean and Drake, Richard M. 27 July 1961. Bimonthly Report No. 1, 12 May - 11 July 1961. (AD-261518). Contract NOw 61-0676-c.

The preparation and growth of crystals of SiC in solid solution with B is well advanced. Up to about 4-5 weight-percent B will go into solid solution with SiC. The amount of B present in the SiC is independent of the initial form of the B. B has been added to SiC, prior to heating, in the form of BN, B₄C, B₂O₃, and elemental B. In each case, the limit of 4.5 percent B was not exceeded. Nitrogen analyses indicate a variation in N content from experiment to experiment, but no correlation can be made between B content and N content.

23. Carborundum Co., Niagara Falls, New York.
A STUDY OF FUNDAMENTAL MECHANICAL PROPERTIES OF CERAMIC SINGLE CRYSTALS. Batha, H. Dean and Drake, Richard M. 21 September 1961. Bimonthly Report No. 2, 12 July - 11 September 1961. (AD-264351). Contract NOw 61-0676-c.

The three-point bending apparatus for obtaining stress-strain curves is nearly complete. This will measure Poisson's Ratio, Young's Modulus, modulus of rupture, and toughness for each crystal. Small crystals of a solid solution of aluminum nitride and silicon carbide have been grown and a furnace for experimenting with the growth of massive crystals from the vapor phase is being built.

24. Carborundum Co., Niagara Falls, New York.
MECHANICAL PROPERTIES OF SILICON CARBIDE SINGLE CRYSTALS. Batha, H. D. and Hasselman, D. P. H. September 1962. Final Report, 12 May 1961 - 12 August 1962. Contract NOw 61-0676-c.

This project was initiated to investigate the mechanical properties of vapor-phase grown single crystals of silicon carbide. Equipment was designed to deform the crystals in bending by three-point loading. Preliminary results for Young's modulus of elasticity and cross-bending strength are reported. Values of strength as high as 1 million psi were obtained. A correlation was found between sample thickness and strength. The strength of 1750°C considerably exceeds the strength at room temperature. No evidence of gross plastic deformation under mechanical load was found as high as 1800°C. Some observations were made of dislocation motion during etching at 900°C in borax.

25. Carborundum Co., Niagara Falls, New York.
STUDY OF FUNDAMENTAL MECHANICAL PROPERTIES OF CERAMIC SINGLE CRYSTALS. Batha, H. Dean. 1962. U. S. Government Research Reports, Vol. 37, No. 8. (AD-271385).

The three-point bending apparatus for obtaining stress-strain curves is assembled and preliminary testing is underway. Preliminary measurements on MgO crystals appear to agree with published values. Apparatus for cutting single crystals of SiC was built and tested.

26. Carborundum Co., Niagara Falls, New York.
PROCESS FOR ADJUSTING THE ELECTRICAL CHARACTER-
ISTICS OF SILICON CARBIDE CRYSTALS. Carroll, P. E.
U. S. Patent 3,074,887 issued 22 January 1963.

The preparation of low resistivity SiC is discussed. The resistivity of colorless SiC can be reduced by heating the semiconductor above 1500°C but below the recrystallization temperature (2150° - 2200°C) in an atmosphere of nitrogen, hydrogen, or argon. Good results are obtained at about 1950°C. The resistivity of colorless SiC can also be reduced by heat treatment in an argon atmosphere containing vaporized phosphorus or in the presence of free silicon. The resistivity of green silicon carbide can be reduced by heat treatment in a nitrogen atmosphere.

27. Carborundum Co., Niagara Falls, New York.
A STUDY OF FUNDAMENTAL MECHANICAL PROPERTIES
OF CERAMIC SINGLE CRYSTALS. Shaffer, P. T. B. and
Batha, H. D. 25 March 1963. Bimonthly Progress Report
No. 1, 14 January - 14 March 1963. (AD-402116). Contract
N600(19)-59749.

Measurement of cross-bending strength and Young's modulus of pure silicon carbide was carried out on approximately 25 samples at room temperature.

28. Carborundum Co., Niagara Falls, New York.
A STUDY OF FUNDAMENTAL MECHANICAL PROPERTIES
OF CERAMIC SINGLE CRYSTALS. Shaffer, P. T. B. and
Batha, H. D. 22 May 1963. Bimonthly Progress Report No.
2, 15 March - 14 May 1963. (AD-410440). Contract N600
(19)-59749.

Additional data on strength and elastic properties of boron-doped silicon carbide crystals were obtained on thin crystals. Analyses are being made to determine the specific effect of impurities on strength.

29. Carborundum Co., Niagara Falls, New York.
A STUDY OF FUNDAMENTAL MECHANICAL PROPERTIES
OF CERAMIC SINGLE CRYSTALS. Shaffer, P. T. B.
Bimonthly Progress Report No. 4, 15 July - 14 September
1963.

Microhardness measurements show that boron additions do not increase the microhardness of single crystal silicon carbide. Etching studies, to remove surface defects leading to low strengths of single crystals, have been initiated to find a means of improving the overall strength of being evaluated statistically by means of a computer program.

30. Carborundum Co., Niagara Falls, New York.
A STUDY OF FUNDAMENTAL MECHANICAL PROPERTIES OF CERAMIC SINGLE CRYSTALS. Liebling, R. S. 27 November 1963. Bimonthly Progress Report No. 5, 15 September - 14 November 1963. (AD-427371). Contract N600(19)-59749.

Load capacity of bar shaped silicon carbide single crystals varies inversely with the length width ratio and boron concentration. As thickness increases, load capacity increases. The effects of temperature, thickness, length, width, boron concentration, and surface treatment are being thoroughly analyzed using data processing equipment. Future research will concentrate on chemical polishing with chlorine gas, oxygen, $\text{KNO}_3 + \text{KOH}$, and borax. Electrolysis in water and molten NaOH will also be studied as possible polishing techniques.

31. Centre d'Etude de l'Energie Nucleaire, Mol, Belgium.
SOLID STATE NEUTRON DETECTOR. Final Report, 1962. Work performed under United States - Euratom Joint Research and Development Program. Contract 079-61-10-RDB.

A neutron detector is developed for the detection of high neutron fluxes at high temperatures, using silicon carbide as the base material. Silicon carbide p-n junctions maintain their rectifying properties at 500°C and develop a rather high photovoltage under gamma radiation. An extensive series of tests performed on the silicon carbide crystal are included.

32. Choyke, W. J. and Patrick, L.
ABSORPTION OF LIGHT IN ALPHA SiC NEAR THE BAND EDGE. Physical Review, Vol. 105, No. 6, pp. 1721-1723. 15 March 1957.

The absorption in alpha SiC of photons of energy 2.6 electron volts to 3.3 electron volts has been measured at temperatures from 77°K to 717°K. The measurements show that the interband transitions are indirect, requiring the absorption or emission of a phonon of energy 0.09 electron volt. The minimum energy gap is found to be 2.86 electron volts at 300°K, and above this temperature $dE_G/dT = -3.3 \times 10^{-4}$ electron volt per degree.

33. Choyke, W. J., Hamilton, D. R., and Patrick, L.
POLARIZED EDGE EMISSION OF SiC. Physical Review,
Vol. 117, No. 6, pp. 1430-1438. 15 March 1960.

The photoluminescence of some relatively pure hexagonal SiC crystals (polytype 6H) includes a strongly polarized edge emission. Two distinct patterns of edge emission lines have been found, but never in the same crystal. In either type, the edge emission includes several narrow lines (half-width $\sim kT/4$ at 77°K) and a number of wider bands spaced at regular energy intervals of 0.03 electron volt, suggestive of a vibrational interaction. Some lines, found in the 77°K edge emission spectrum, vanish at 4°K. Mechanisms for producing polarized light are discussed, and it is concluded that the most probable luminescence centres are donor-acceptor pairs. The two types of spectra may be attributed to two different pairs. Intrinsic recombination radiation was looked for but was not found.

34. Clevite Corporation, Cleveland, Ohio.
METHOD OF GROWING SILICON CARBIDE CRYSTALS.
Shockley, William. U. S. Patent 3,053,635 issued 11 September 1962.

The method comprises forming a bath of carbon and silicon dissolved in a molten solvent which dissolves an appreciable quantity of silicon carbide at below the solvent's vaporization temperature and which has an increasing solubility of silicon carbide with increasing temperature, the solubility process being reversible, maintaining the bath at a molten temperature, adjusting the concentration of the carbon and silicon until the bath is at a saturation point for silicon carbide, inserting a silicon carbide crystal seed into the molten bath, and withdrawing it, the seed serving to cool a surrounding portion of the bath to form a portion supersaturated with silicon carbide which precipitates on the seed as it is withdrawn from the solution.

35. Cornell Aeronautical Laboratory, Inc., Buffalo, New York. GROWTH AND MECHANICAL PROPERTIES OF FILAMENTARY SILICON CARBIDE CRYSTALS. Yerkovich, Luke A. and Kirchner, Henry P. August 1961. Report No. WADD TR 61-252. (AD-273997). Contract AF 33(616)-7005.

In this investigation, silicon carbide whiskers were grown under various experimental conditions. The strength and modulus of elasticity of several whiskers were determined at room temperature. Methods of heating the whiskers for high-temperature measurements were investigated. The specific gravity of the whiskers has been inferred from measurement of the unit cell dimensions by X-ray diffraction patterns. Silicon carbide whiskers were grown by pyrolysis of methyl-richlorosilane in hydrogen. In some cases, dense growths of whiskers from 1.2 to 1.5 centimeters in length and from 2 to 5 microns in diameter were observed. The longest whisker obtained, thus far, was 5 centimeters.

36. Dalvan, R. ABSORPTION EDGE IN β -SILICON CARBIDE. Journal of Physics and Chemistry of Solids, Vol. 13, No. 1-2, pp. 163-164. May 1960.

Optical absorption of β -SiC at room temperature is reported for photon energies of 2.3 to 2.9 electron volts. The results indicate an optical energy gap of 2.2 ± 0.1 electron volts.

37. Dillon, J. A., Jr., Schiler, R. E., and Farnsworth, H. E. SOME SURFACE PROPERTIES OF SILICON-CARBIDE CRYSTALS. Journal of Applied Physics, Vol. 30, No. 5, pp. 675-679. May 1959.

The work functions of a number of commercial-grade silicon-carbide single crystals were obtained in high vacuum ($p < 10^9$ millimeter of mercury). Low-energy electron-diffraction studies were also made for one of these samples. Surfaces cleaned by argon-ion bombardment and annealing appeared to contain an excess of carbon. Heating for long periods of time at 1000°C also appeared to produce surfaces which were non-stoichiometric. Oxygen was adsorbed at room temperature on the ion-bombardment cleaned surfaces with a sticking coefficient of the order of 0.01. Differences in adsorption properties were noted which were probably associated with asymmetry in atomic species on different crystal faces. Work-function

values on opposite faces of any crystal were the same. Hydrogen exposure resulted in work-function decreases only in the presence of a heated filament. Under similar conditions of ion bombardment and high-temperature heating, the SiC surfaces appeared to be more stable than those of silicon crystals.

38. English, A. C. and Drews, R. E.
SPACE-CHARGE-LIMITED CURRENTS IN SILICON CARBIDE SINGLE CRYSTALS. Scientia Electronica, Vol. 9, No. 1, pp. 1-25. 1963.

Thin high-resistivity silicon carbide crystals with alloyed tungsten contacts show space-charge-limited current behavior at 77°K. There is strong evidence of trapping effects, apparently from levels lying at about 0.2 electron volt from the valence band, in concentration of about 10^{13} cm^{-3} . The effect of poorly rectifying contacts and of bands of trapping levels on the analysis is discussed. Simplified space-charge-limited current theory is extended to two discrete trapping levels and to a band of levels.

39. Drowart, J., De Maria, G., and Inghram, M. G.
THERMODYNAMIC STUDY OF SiC UTILIZING A MASS SPECTROMETER. Journal of Chemical Physics, Vol. 29, No. 5, pp. 1015-1021. November 1958.

The sublimation of hexagonal SiC has been studied under equilibrium conditions. The predominant gaseous species above SiC are Si, SiC₂, and Si₂C. By combining the heat of formation of gaseous Si from solid SiC and the known standard heat of formation of SiC, a value of 113 kcal/g atom is obtained for the heat of sublimation of Si at 298°K. From the measured partial pressures, using estimated free energy functions, dissociation energies for Si₂, Si₃, SiC, SiC₂, Si₂C, Si₂C₂, Si₂C₃, and Si₃C are calculated and compared with previously known dissociation energies for group IVB molecules.

40. Ehrlich, G., Gerbatsch, R., and Freitag, G.
SPECTROGRAPHIC DETERMINATION OF TRACE IMPURITIES IN SILICON CARBIDE. Chemia Analityczna, Warsaw, Vol. 7, No. 2, pp. 435-443. 1962. (In German).

A grating spectrograph (652 lines per millimeter) was used, with a 10-ampere dc arc and an exposure time of 90 seconds.

Standards containing 0.1 to 30 parts per million of Al, Ca, Cu, Mg, Mn, Ti, and V were prepared by mixing the required amounts of each element (in solution as nitrate; Ti and V as oxide) with carbon and then mixing the product with powdered pure silicon in the proportion 3 to 7. The reproducibility was ≈ 10 percent, and limits of detection were estimated. Accuracy was difficult to assess, e. g., the Cu contents of two samples as determined by activation analysis (8 parts per million) were lower than those found spectrographically (13 and 18 parts per million), possibly owing to inhomogeneity in the samples.

41. Electronic Technology Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.
SILICON CARBIDE RECTIFIERS. Maiden, C. E. Report on Secondary Power Transmission Utilization. May 1959. WADC Technical Note No. 59-162. (AD-216087).

The forward and reverse dc measurements of silicon carbide rectifiers were measured and the rectifying characteristics of the units were photographed. The rectifiers tested are interim samples from a development contract and were evaluated at 25°, 200°, 300°, 400°, and 500°C. The test results indicate a substantial increase in the state-of-the-art of solid-state rectifiers for high-temperature applications.

42. Electrotechnical Laboratory, Industrial Science and Technology Agency, Tokyo, Japan.
EXPERIMENTAL STUDY ON THE SILICON CARBIDE NON-LINEAR RESISTORS. Tsurumi, Sakuro. September 1961. Report in Japanese. Synopsis in English.

This paper describes the results of experimental studies on silicon carbide nonlinear resistors. A historical review of silicon carbide is presented and recent theories advanced on the electrical conduction phenomena of the silicon carbide contacts are briefly described. Experimental studies on the manufacture of the lightning arrester characteristic element are described. Processing conditions considered include the effect of the grain size of the silicon carbide crystals, the contents of the binding materials, and the firing conditions. The optimum conditions were obtained with the grain size of Number 120 mesh SiC, with 15 to 20 percent binding materials, and with firing temperatures of 900° to 1000°C.

The problem of the absorption of humidity by nonlinear resistors was treated and a new method of detecting the water content was presented. The application of the impulse current on nonlinear resistors results in the change of electrical characteristics of the resistors, particularly in the range of low current densities. These phenomena can be used to stabilize the character of the resistors and to adjust the electrical characteristics of the nonlinear resistors to a desired value. Also, the application of nonlinear resistors for spark suppression of electric contacts was treated. Problems concerning the practical design of contact protection were studied, and the effectiveness of the formulae was confirmed by experiment.

43. Flowe, L., Thompson, H. D., and Cali, J. P.
NEUTRON ACTIVATION ANALYSIS OF SILICON CARBIDE.
Analytical Chemistry, Vol. 31, No. 12, pp. 1951-1953. 1959.

A method is described for determining impurities in the parts per 10^9 range or less. After irradiation with thermal neutrons, the sample is decomposed with chlorine and oxygen at 1250° . Standard radiochemical procedures are then used for separating and measuring the induced activities. Inconsistencies found in analyses are much greater than the uncertainty of the measurements and indicate a nonhomogeneous distribution of impurities.

44. General Electric Company, Schenectady, New York.
METHOD OF MAKING SILICON CARBIDE. Prener, Jerome S.
U. S. Patent 3,085,863 issued 16 April 1963.

The process includes adding silicon tetrachloride to a sugar solution to form a silica gel, dehydrating the gel to decompose the sugar and form a homogeneous finely-divided mixture of silica and carbon, and heating the mixture in an inert atmosphere to form silicon carbide.

45. General Electric Company, Ltd., Research Laboratories,
Wembley, England.
RESEARCH ON TRANSISTORS AND SEMICONDUCTORS.
Progress Report No. 7. Jonscher, A. K. 15 November 1960.
Report No. 13756C. (AD-246858).

No abstract.

46. General Electric Company, Ltd., Research Laboratories, Wembley, England.
C. V. D. RESEARCH PROJECT RP3/38. SILICON CARBIDE. Progress Report No. 1. Brander, R. W. and Martin, J. R. 23 November 1961. Report No. 14056C. (AD-268242).

Single crystals of SiC of good purity and crystal perfection were grown using a vapor-phase technique. Methods of growing from a solution of C in a Si melt also were investigated. Devices capable of rectifying at 500°C were produced. The rectifying characteristics depend markedly on the resistivity and perfection of the starting materials; these control, respectively, the forward and reverse characteristics. Techniques developed in the production of these devices are described. These include alloying, etching, mounting, bonding of lead wires, and encapsulation.

47. General Electric Company, Ltd., Research Laboratories, Wembley, England.
C. V. D. RESEARCH PROJECT RP3/38. THE GROWTH OF SILICON CARBIDE FROM MOLTEN SILICON. Beckmann, G. E. J. 27 November 1961. Report No. 14021C, (AD-270151).

Synthesis of SiC is reported from graphite and molten Si throughout the temperature range 1450° to 2600°C. The Si was held in nonuniformly heated graphite crucibles. The extent of the crystallization-conversion of up to one-third of the Si into SiC at 2300°C greatly exceeded that to be expected from the low solubility of C in Si. This result is attributed to rapid cycling of the solution between regions differing in temperature with consequent supersaturation and crystallization in the cooler regions. This mechanism was applied to the production of pure polycrystalline cubic SiC in the range 2100° to 2600°C.

48. General Electric Company, Ltd., Research Laboratories, Wembley, England.
C. V. D. RESEARCH PROJECT RP3/38. SILICON CARBIDE. Progress Report No. 2. Brander, R. W. and Martin, J. R. 11 December 1962. Report No. 14285C. (AD-294374).

Improvements in the quality and size of single crystals grown from the vapor phase have been achieved, and a better understanding of growth conditions has been obtained. Investigations into the effect of starting material stoichiometry and the effect

of impurity on the growth process and the resulting material quality are being carried out, and some preliminary results are reported. Some qualitative results on diffusion are given and the discovery of a new etch, giving a smooth surface, is recorded. Single-crystal epitaxial layers have been grown from a solution of carbon in molten silicon, and from silicon and vapors in an open tube. Both methods have resulted in grown layers of reasonable thickness and quality, and of the same polytype as the seed crystal. In the vapor-phase technique, one (0001) face grows at twice the rate of the other, further emphasizing the asymmetry already observed in etching experiments.

49. General Electric Company, Ltd., Research Laboratories, Wembley, England.
C. V. D. RESEARCH PROJECT RP3/38. EPITAXIAL GROWTH OF SILICON CARBIDE. Brander, R. W. 28 August 1963. Report No. 14431C. (AD-423334).

The growth of single-crystal layers of various polytypes on alpha-SiC seeds was carried out by a vapor-phase process using elemental silicon and carbon sources. The growth rates on opposite (0001) substrate surfaces were found to differ by a factor of two, although the quality of growth appears identical. Layers grown above 1900°C show continuity of polytypism with the substrate. Below 1900°C, different polytypes may grow.

50. General Electric Company, Ltd., Great Britain.
CRYSTALLINE SILICON CARBIDE. Beckmann, George E. J. British Patent 967,933 issued 26 August 1964. Applied 23 October 1961.

Si is melted in a crucible of high-d, graphite (e.g. 1.83 grams per cubic centimeter) in an induction furnace. The temperature at the central part of the crucible is ~2300°; the temperature at the top and bottom is ~1800°. Heating is continued for ~20 minutes, followed by cooling to room temperature. The reaction mass is treated with a 50-50 mixture of HNO₃ and HF to dissolve Si, leaving crystallized SiC, suitable for use in semiconductors.

51. General Electric Company, Schenectady, New York.
SILICON CARBIDE DIODE "LASER." Hall, R. N. In its Semiconduction Device Concepts, pp. 47-58. 31 October 1963.

Luminescence from travelling solvent SiC diodes is discussed. It is concluded that the narrow emission line which has been reported is due to the spontaneous recombination of bound excitons and is unrelated to coherent light emission.

52. Gilman, J. J.
THE ART AND SCIENCE OF GROWING CRYSTALS. John Wiley and Sons, Inc., New York. 1963.

No abstract.

53. Goffaux, R.
PROPERTIES OF SILICON CARBIDE UNDER THE ACTION OF ELECTRIC PULSES. Revue Generale D Electronique, Vol. 66, No. 9, pp. 463-472. September 1957. (In French).

The nonlinear behavior of SiC complexes under the action of very high electric fields, as for example in their use as lightning surge arresters for power lines, has been discussed by Busch and Teszner. The experiments described here show that the hysteresis observed in the current-voltage characteristic is a function of the duration of the applied high-voltage impulse, being less for shorter pulses. The experimental data can all be explained in terms of a new theory which depends on a new model for the material surrounding the grains of SiC and which is responsible for the intergranular barriers.

54. Goffaux, R.
ELECTRICAL PROPERTIES OF SILICON CARBIDE. INTERPRETATION OF THE DYNAMIC CHARACTERISTIC. THEORY OF NON-OHMIC RESISTANCE. Revue Generale D Electronique, Vol. 66, No. 11, pp. 569-576. November 1957. (In French).

For previous work, see preceding abstract. The semiconducting layer around the SiC granules is supposed to contain a series of trapping levels about 0.15 electron volt below the conduction band and a series of donor centers about 0.35 electron volt below the conduction band and just above the Fermi level. The time constants for the increase in the carrier concentration on the application of a high field (calculated by the author) is found to agree with values deduced from measurements of Debye absorption. The theory when applied to the small-current part of the V-I characteristic also shows good agreement with the measured dc conductance.

55. Gorban', I. S. and Rud'ko, S. N.
OPTICAL PROPERTIES OF SILICON CARBIDE CRYSTALS.
Soviet Physics-Solid State, Vol. 5, pp. 995-998. November
1963. (A translation).

The structure of the long-wavelength fundamental absorption edge, the ultraviolet spectrum, and the properties of photoluminescence of synthetic and technical-grade silicon carbide crystals have been investigated. The structure of the edge is ascribed to indirect transitions with participation of three types of phonon. The properties of the absorption spectrum in the ultraviolet indicate the complex structure of the electron bands. It is found that silicon carbide crystals exhibit photoluminescence of two types which differ in the energy distribution in the spectrum, the temperature dependence of the intensity, and in the excitation spectra.

56. Gorin, S. N. and Pletyushkin, A. A.
STRUCTURAL CHARACTERISTICS OF CUBIC SILICON
CARBIDE CRYSTALS GROWN FROM THE VAPOR PHASE.
Akademii Nauk SSSR. Izvestiya, Seriya Fisicheskaya, Vol. 28,
No. 8, pp. 1310-1315. 1964. (In Russian).

Crystals of β -SiC (cubic) were grown by thermal decomposition of MeSiCl_3 in H_2 at 1500° to 2000° . The crystals were subjected to X-ray, optical goniometric, and etching (by KOH at 500°) experiments. Single crystals were of a platy habit, while prismatic crystals grew twinned parallel to the $\{111\}$ planes. The structural polarity in the $\langle 111 \rangle$ direction was noted to affect the growth habit of the crystals. The absorption of impurities, including N, B, and Al, was also correlated to polarity in the $\langle 111 \rangle$.

57. Greebe, C. A. A. J. and Knippenberg, W. F.
GROWN P-N JUNCTIONS IN SILICON CARBIDE. Philips
Research Report, Vol. 15, No. 2, pp. 120-123. April 1960.

An account is given of the preparation and properties of grown junctions. The forward characteristics are tentatively explained on the basis of a p-i-n structure. P-n luminescence has been observed containing violet light.

58. Green, G. W., Hogarth, C. A., and Johnson, F. A.
SOME OBSERVATIONS OF THE EFFECTS OF OXYGEN ON
THE MINORITY CARRIER LIFETIME AND OPTICAL ABSORP-
TION OF SILICON CRYSTALS PULLED IN VACUO. Journal
of Electronics and Control, Vol. 3, No. 2, pp. 171-182.
August 1957.

The techniques and the equipment used for producing single crystals of silicon by pulling from a melt in vacuo are described and some electrical characteristics of crystals so grown are reported. The minority carrier lifetime decreases radially from the center of the crystals and this behavior is believed to arise from a difference in oxygen concentration, being greater near the axes of the crystals and smaller towards the edges. Optical absorption measurements, which indicate the relative concentrations of oxygen in silicon crystals grown by various techniques, suggest that while there is a low concentration in vacuum-grown crystals, there is still a radial variation as postulated above. The oxygen is believed to reside at dislocations where it is held at SiO_2 and thus relieves the local strain fields.

59. Griffiths, L. B., Mlavsky, A. I., Rupprecht, G., Rosenberg, A. J., Smakula, P. H., and Wright, M. A.
SILICON CARBIDE DIODE LASER. IEEE Proceedings, Vol. 51, pp. 1374-1376. October 1963.

Description of stimulated emission observed from forward-biased p-n junctions in α -SiC fabricated by a new solution growth technique. The emission peaks at 4560 \AA (2.72 electron volts) with a linewidth which is less than 5 \AA (resolution limit of the spectrometer). Continuous operation has been observed at room temperature above threshold current densities as small as $120 \text{ amperes per centimeter}^2$. Spatial coherence of the radiation has been established by photographic evidence of constructive interference.

60. Hall, R. N.
ELECTRICAL CONTACTS TO SILICON CARBIDE. Journal
of Applied Physics, Vol. 29, No. 6, pp. 914-917. June 1958.

Rectifying junctions may be made by heating silicon-aluminum or silicon-boron alloys in contact with n-type silicon carbide. The measured solubility of carbon in liquid silicon is consistent with the view that these junctions are produced by an alloying and regrowth mechanism. Nonrectifying contacts may be made in an analogous manner using silicon-phosphorous alloys. Visible radiation is emitted uniformly over the rectifying junctions when current is passed in the forward direction, with a quantum efficiency of the order of 10^{-6} . Current flow in the reverse direction is associated with the appearance of blue spots, similar in appearance to the points of light that are often observed when silicon junctions are biased in the avalanche region.

61. Hamilton, D. R.
INTERFEROMETRIC DETERMINATION OF TWIST AND
POLYTYPE IN SILICON CARBIDE WHISKERS. Journal of
Applied Physics, Vol. 31, pp. 112-116. January 1960.

Observation of a twist in the $\{1\bar{1}00\}$ faces of hexagonal SiC whiskers by means of optical interference techniques is reported. The whiskers were grown in a graphite tube furnace by sublimation of SiC in hydrogen and were deposited at temperatures about 2000°C as acicular crystals of hexagonal section with $\{0001\}$ along the whisker length. The Eshelby formula for twist caused by a screw dislocation has been used to estimate the strength of the associated Burgers vector. It is found that, within the experimental error, the estimated Burgers vector is equal to, or is an integral multiple of, the unit cell of the SiC polytype 4H. It is concluded that these twisted whiskers grow by means of a screw dislocation of integral strength parallel to the axis, and that they are of polytype 4H.

62. Hamilton, D. R., Choyke, W. J., and Patrick, L.
PHOTOLUMINESCENCE OF NITROGEN-EXCITON COMPLEXES
IN 6H SiC. Physical Review, Vol. 131, pp. 127-133. 1 July
1963.

The photoluminescence of n-doped 6H SiC reveals two distinct edge emission spectra, a consequence of the existence of two kinds of nitrogen-exciton complexes. The recombination radiation of excitons bound to nitrogen ions is described, complementing the previously reported recombination radiation of excitons bound to neutral nitrogen. By combining data from the two spectra, estimates of the ionization energies of 0.17,

0.20, and 0.23 electron volt, for the three inequivalent nitrogen donors are obtained. Several phonon energies can be determined, and these are compared with known phonon energies in 6H SiC. A 90-million electron volts phonon apparently represents a localized vibrational mode. Quenching of edge emission in impure samples is observed, and is attributed to exciton hopping. Thermally excited states of the nitrogen-exciton complexes appear to be due to the valley-orbit splitting associated with a sixfold conduction-band degeneracy. A splitting of some of the states is attributed to the John-Teller effect.

63. Hancock, R. D. and Edelman, S.
SIMPLIFIED LIGHT REFLECTION TECHNIQUE FOR ORIENTATION OF GERMANIUM AND SILICON CRYSTALS. Review of Scientific Instruments, Vol. 27, No. 12, pp. 1082-1083. December 1956.

A collimated light beam 0.075 inch diameter from a zirconium arc falls on the etched surface of the hemispherically ground end of the semiconductor ingot placed behind a thin glass plate. The latter reflects the light beam back onto the light entrance hole in a viewing screen perpendicular to the beam. Movement of the ingot allows focusing and location of the reflected image for symmetry. Basic patterns related to orientation are obtained and can be recognized with little difficulty.

64. Hardeman, G. E. G.
ELECTRON AND NUCLEAR SPIN RESONANCE IN n-TYPE SILICON CARBIDE. Journal of Physics and Chemistry of Solids, Vol. 24, pp. 1223-1231. October 1963.

The electron nuclear double resonance in n-type silicon carbide at low temperatures is discussed. The magnetic interaction between the bound donor electron and the ^{29}Si and ^{13}C nuclei has been studied by this method. Transitions of the lattice nuclei interacting with the donor electrons cause some change of the level of the electron spin resonance. By means of this effect (ENDOR), the nuclear magnetic resonance of the nuclei surrounding the donor centers has been detected. The nuclear resonance frequency is shifted, due to the bound donor electron, the shift being dependent on the position of the nucleus with respect to the center.

65. Hasselman, D. P. H. and Batha, H. D.
STRENGTH OF SINGLE-CRYSTAL SILICON CARBIDE.
Applied Physics Letters, Vol. 2, No. 6, pp. 111-113. 1963.

The tensile strength and Young's modulus were determined on whiskers grown from the vapor phase by using a bending jig. The tensile strength was inversely proportional to the thickness and at 1750° was about 5 times larger than that at room temperature for a given thickness. Theoretical strengths of nearly 650,000 psi were found in some specimens at the higher temperature. No evidence of plastic deformation was found.

66. Hori, Jun.
GROWTH PATTERNS ON SiC SINGLE CRYSTALS. Review of the Electrical Communications Laboratory, Tokyo, Vol. 10, No. 11-12, pp. 587-596. 1962.

The various types of spiral patterns on the surface of α -SiC single crystals are observed in detail, and the growth velocity, supersaturation ratio, and step height of the crystals are established. SiC is one of the typical crystals which show various complicated modifications. On the surfaces of the crystals, clear growth spirals are frequently observed. The observation of the surface patterns gives important information on the growth mechanism. SiC, which is the bonding intermediate between homopolar and heteropolar, occurs in the cubic form β -SiC and the hexagonal varieties grouped as α -SiC. Many-stepped spiral dislocations, characteristic of SiC crystals, were observed on the hexagonal faces when examined microscopically. Upon the growth of a crystal face from vapor, dislocation will be formed in a crystal by the formation of 2-dimensional nuclei. From photographic observations of the radius of the critical nucleus, the supersaturation and the d. of dislocations can be established.

67. Kawamura, Tsutomu and Hayashi, Kazuo.
PREPARATION OF SILICON CARBIDE SINGLE CRYSTALS.
Journal, Physical Society of Japan, Vol. 17, pp. 1517-1518. 1962.

SiC single crystals with planar surfaces (hexagonal platelets) and a length of 3-5 millimeters (maximum 10 millimeters) were grown at 2500° to 700° by the sublimation method. The crystals were colorless to light green. The colorless crystals

were p-conducting, had a charge-carrier concentration of 10^{15} per cubic centimeter and a charge carrier mobility of ~ 50 centimeter² per volt-second.

68. Kern, B.
THE Si $K\beta$ -BANDS OF THE X-RAY EMISSION SPECTRA OF
ELEMENTARY Si, SiC and SiO₂. Zeitschrift for Physik,
Vol. 159, No. 2, pp. 178-193. 1960. (In German).

The Si $K\beta$ -emission bands of silicon, carborundum, and quartz, hitherto unknown or known inaccurately, were photographed using a high-dispersion focusing spectrograph. The results are presented in the form of photometer curves and in a table giving the energy values for structural features. For all three, all emission bands of the elements concerned are now known. A comparison of the emissions, together with that from diamond, indicates that the spectra essentially represent the form of the energy bands of the valency electrons and that they are little influenced by unusual excited states. The emission bands of silicon, carborundum, and diamond show to a great extent similar features, thereby indicating an essentially covalent type of bonding in all cases including carborundum. The emission forms are in rough agreement with the calculated valency band structures.

69. Kharlamova, T. E. and Kholuyanov, G. F.
ELECTRICAL PROPERTIES OF ALLOYED P-N JUNCTIONS
IN SILICON CARBIDE. Soviet Physics-Solid State, Vol. 2,
pp. 397-402. September 1960. (A translation).

An investigation of the current-voltage characteristics of silicon carbide p-n junctions in the temperature range from 20° to 500°C is reported. The junctions were obtained by alloying an aluminum-silicon alloy in a hydrogen atmosphere to n-type crystals of silicon carbide with a resistivity of 2 to 2.5 ohm-centimeters. On the basis of measurements of the dependence of the recombination radiation intensity on the voltage, laws governing the increase of the diffusion component of the current, as a function of the voltage increase in the forward direction, have been found. The diffusion length of holes is estimated from the time constant of the recombination radiation decay. It is shown that the leakage affects the current-voltage curves of p-n junctions. In the entire range of the investigated voltages, the growth of the inverse current with the voltage was greater than linear. At high inverse voltages,

phenomena which indicate that avalanche breakdown takes place along the periphery of a p-n junction and in the vicinity of defects have been observed. The capacitance of the p-n junctions and its dependence on the voltage and the temperature have been measured. The possibility of using p-n junctions in silicon carbide as nonlinear capacitors is discussed.

70. Kholuyanov, G. F.
PHOTOELECTRIC PROPERTIES OF ALLOY P-N JUNCTIONS
IN SILICON CARBIDE. Soviet Physics-Solid State, Vol. 2,
pp. 1722-1726. February 1961. (A translation).

Photoelectric response characteristics of alloy p-n junctions in alpha-SiC are evaluated. Illumination was from the p-side of the junction. At room temperature, maximum response is for photon energy ranging from 4.3 to 4.5 electron volts; increasing the temperature shifts the response towards lower photon energy values, accompanied by a reduction in the forbidden bandwidth. Short-circuit currents rise linearly with increasing temperature. The photo-electro motive force at room temperature is 1.2 volts for an illumination of 5 milliwatts per centimeter². Reasons for the low photosensitivity of this compound are discussed.

71. Kirchner, Henry P. and Knoll, Peter.
SILICON CARBIDE WHISKERS. Journal of American Ceramic Society, Vol. 46, pp. 299-300. 1963.

Elongated crystals of SiC were prepared by decomposition of MeSiCl₃ in H₂. Data are presented on tensile strength, Young's modulus, and electric resistivity.

72. Kleber, W. and Jegerlehner, J.
GROWING OF SILICON CARBIDE SINGLE CRYSTALS BY
THERMAL DECOMPOSITION OF SILICON TETRACHLORIDE
AND TOLUENE. Zeitschrift Fuer Physikalische Chemi.
Leipzig, Vol. 223, No. 1-2, pp. 1-7. 1963. (In German).

Based on the method by Kendall (J. Chem. Phys. 21, 821(1953)) SiC single crystals were prepared by thermal decomposition of SiCl₄ and toluene on a C filament at 2000° to 300°. The crystal product chiefly consists of cubic β -SiC. By modification of the method (use of a C rod) the growth conditions could be improved considerably. The β -SiC crystals are morphologically well developed and showed the combination (100) + (111)

and $(\bar{1}\bar{1}1)$, respectively. The tristetrahedron (115) could also be observed goniometrically. On the cube and tetrahedron planes, a characteristic striation parallel to (110) was found which is probably due to inclusions of α -SiC lamellas with (0001) parallel to the tetrahedron planes of the cubic SiC. Besides the cubic modification, hexagonal α -SiC crystals with 4-H structure could also be detected. The formation of graphite whiskers in the growth method is described.

73. Knippenberg, W. F., Haanstra, H. B., and Dekkers, J. R. M. CRYSTAL GROWTH OF SILICON CARBIDE. Phillips Technical Review, Vol. 24, pp. 181-183. 1962-1963.

Reported are results of an electron microscope investigation of the growth of SiC crystals at the earliest stages, consisting in the formation of whiskers with hexagonal structure. Some are tapered, needle-shaped of hexagonal cross section; some are greatly elongated platelets. On larger specimens, visible under the light microscope, alternating cubic and hexagonal parts could be distinguished along the whiskers.

74. Knippenberg, W. F., Haanstra, H. B., and Dekkers, J. R. M. GROWTH OF SILICON CARBIDE CRYSTALS. Engineers' Digest, Vol. 24, pp. 87-88. June 1963.

Details are given of the results of a microscopic investigation into the initial stage in the growth of silicon carbide crystals from a reaction between carbon and quartz sand at 1500°C. This initial stage comprises the formation of whiskers of different types, several of which are described and illustrated.

75. Knippenberg, W. F. GROWTH PHENOMENA IN SILICON CARBIDE. Philips Research Report, Vol. 18, pp. 161-274. June 1963.

The growth of crystalline SiC and the polymorphism of this substance are discussed. The growth was studied by performing chemical reactions and subjecting the reaction products to heating procedures. The influences of impurities on the growth process and the phase transitions occurring upon heating were examined. The different polymorphic forms of silicon carbide were found to show the same relation between habitus and temperature. At low temperatures the crystals are predominantly acicular, at higher temperatures they possess a lamellar form. Parallel growth of a number of lamellae

results in the formation of tabular and wedge-shaped crystals. In a temperature gradient, a crystal grows in such a way that the polar axis of the tetrahedral structure assumes a definite orientation. When a wedge-shaped crystal is formed in a temperature gradient, the individual lamellae grow in length one after another towards the highest temperature. Even in an isothermal environment in contact with the equilibrium vapor, polycrystalline silicon carbide develops by surface diffusion into thin lamellae.

76. Kohn, J. A. and Eckart, D. W.
TWINNING STUDY OF CUBIC (β) SILICON CARBIDE.
American Mineralogist, Vol. 47, No. 9-10, pp. 1005-1010.
1962.

The recent emphasis on silicon carbide as a potential high-temperature electronic material has led to improved crystal growth techniques. As a result, well-formed, high-purity, cubic (β) SiC specimens have become available for crystallographic investigations. A study of 25 pure and doped β -SiC crystals by the Weissenberg X-ray method showed prolific twinning (normal and high-order), some stacking randomness, and one case of polytypism (15R). Only two crystals were structurally pure. No clear correlation between these findings and morphology or doping could be established. High-order twinning in β -SiC is discussed, with emphasis on the relation of a multiple-individual, nonparallel, twin complex to its resultant Weissenberg diffractometry.

77. Krishna, P. and Verma, A. R.
A NOVEL DETERMINATION OF THE STRUCTURE OF AN ANOMALOUS POLYTYPE OF SILICON CARBIDE. Acta Crystallographica, Vol. 17, pp. 51-57. January 1964.

An unusual SiC crystal of special crystallographic interest is discussed. During growth a change in the structure occurred from one region of the crystal to another, without a change of space group ($P3m$) or of the dimensions of the unit cell. The crystal has been identified as type 36H (Ramsdell notation) and its two structures, designated as $36H_a$ and $36H_b$, form, respectively, the upper and lower portions of a single crystal piece. In addition to the usual extinctions inherent in all SiC structures, the X-ray diffraction photographs of $36H_b$ show striking structural extinctions. In the 10.1 row, the reflections $l = 6n \pm 2$ (n any positive or negative integer) have zero intensity;

this imposes on the structure, the conditions

$$\sum_{zA} \exp[2\pi i(6n \pm 2)z] = \sum_{zB} \exp[2\pi i(6n \pm 2)z] = \sum_{zC} \exp[2\pi i(6n \pm 2)z] = 0.$$

The polytype has an unexpected structure with the Zhdanov symbol (333334333332), which has been confirmed by agreement between the observed and calculated relative intensities of X-ray reflections. The growth of this structure is discussed with respect to existing theories of polytypism, and it is concluded that none of them is able to provide a completely satisfactory explanation for the growth of the crystal.

78. Kuo, Chang-Lin.
THIRTY-TWO NEW POLYTYPES OF SiC. K'o Hsueh T'ung Pao, No. 1, pp. 78-81. 1964. (In Chinese).

According to the results of X-ray diffraction of > 500 α -SiC crystals by the Laue method, all but four show that these crystal forms are the products of parallel repetition from the fundamental types 6H, 15R, and 4H (Ramsdell notation). By careful analysis of the reciprocal point lattices of the SiC polytypes and those of the 6H, 15R, and 4H types, a method was discovered from their relations to identify the different types of SiC on the basis of the positions of their corresponding points. By this method, 32 new SiC polytypes were found. There are 7 fundamental relations. The relation of any α -SiC with the basic type 6H for the space group R3cm is tabulated, and the 32 new SiC polytypes are also listed.

79. Kuo, Chang-Lin.
TWO NEW POLYTYPES OF SILICON CARBIDE 417R AND 453R. Wu Li Hsueh Pao, Vol. 20, No. 5, pp. 444-456. 1964. (In Chinese).

A detailed study of the relation between diffraction points of various rhombohedral types and the type 6H of SiC was made by using the reciprocal lattice method. Twelve possible relations occur. A method is proposed for determining the number of the h. c. p. layers in the unit cell from the relations derived and the number of points between two Laue points of the type 6H. By using the method proposed, numerous SiC single crystals prepared in the laboratory were analyzed and two new modifications of α -SiC 417R and 453R were found. These two new types are coalescent with the most common type 6H. The

space group of the new types is $R3m-C_3^5$. The unit-cell dimensions in the hexagonal system for 417R and 453R are respectively: 417R: a 3.0806, c 1050.7 Å. and $Z = 417$; 453R: a 3.0806, c 1141.4 Å., and $Z = 453$; and in the rhombohedral unit cell: 417R: a 350.4 Å., α 30.4°, and $Z = 139$; 453R: a 380.6 Å., α 27.8°, and $Z = 151$.

80. Kuo, Chu-Kun and Chen, Hsien-Ch'iu.
THE GROWTH OF β -SILICON CARBIDE CRYSTALS BY THE GAS CRACKING METHOD. K'o Hsueh T'ung Pao, No. 3, pp. 266-269. 1964. (In Chinese).

$SiCl_4$, CH_3SiCl_3 , $(CH_3)_3SiCl$, $CH_3-C_6H_5$ and the carrier gases H, Ar, and N were used to grow SiC under 26 different conditions. Within the temperature range 1400° to 2200°, α - and β -SiC were always found present in the same crystal grains which makes it doubtful that temperature alone is the factor concerned in the transition. α -SiC was only formed if the carrier gas was H. Standard free-energy changes with temperature were calculated for 14 reactions of SiC synthesis. The method of identification and the homogeneity of SiC prepared are also discussed.

81. Liebmann, W. K.
ORIENTATION OF STACKING FAULTS AND DISLOCATION ETCH PITS. Journal of Electrochemical Society, Vol. 111, No. 7, pp. 885-886. 1964.

Straight and triangular stacking faults were observed on a $\{111\}$ β -SiC surface. Along their junction, they form a new fault terminating on both sides with dislocations. Possible orientation of these stacking faults and etch pits are given. The latter are formed by three $\{311\}$ planes which appear to determine the most favorable growth direction.

82. Merz, Kenneth M. and Adamsky, Robert F.
SYNTHESIS OF THE WURTZITE FORM OF SILICON CARBIDE. Journal of the American Chemical Society, Vol. 81, pp. 250-251. 1959.

The thermal decomposition, at 1500°, of CH_3SiCl_3 in H_2 forms SiC, $a = 3.076$, $c = 5.048$ Å, and 2H types; 2-SiC can be grown at temperatures thought to favor β -SiC growth only.

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83. Miller, D. P., Watelski, S. B., and Moore, C. R.
STRUCTURE DEFECTS IN PYROLYTIC SILICON EPITAXIAL
FILMS. Journal of Applied Physics, Vol. 34, pp. 2813-2821.
September 1964.

Metallographic and electron microscopic examination of defects in silicon epitaxial films, grown on silicon wafers on graphite heaters, disclose the origin and characteristics of faults and tetrahedral growths. The occurrence of snowstorm spheres has also been investigated. Silicon carbide has been identified epitaxial on (111) substrates etched in hydrogen. The carbide grows as thin needles against the $\{\bar{1}\bar{1}2\}$ step risers of the $[111]$ zone. The steps appear to be formed during the room temperature oxidation of the silicon wafer surface prior to hydrogen etch. The faults are shown to be twin lamellae resulting from overgrowth of the carbide by the silicon. The methane transport reaction is proposed as the cause of carbide formation. Tetrahedral growths are shown to result from silicon nucleating directly on the carbide away from surface steps. They are twinned to the substrate, and grow faster than the adjacent epitaxial film. Their growth morphology is discussed. The spheres are polycrystalline silicon-silicon carbide matrices apparently resulting from reacted carbon particles which settle upon the substrate at the same time.

84. Minamoto, M.
SURVEY ON SILICON CARBIDE. P. B. Report 140413.
U. S. Government Research Reports, Vol. 32, No. 2. 1959.

A survey of the literature on, and developments in, silicon carbide includes crystallographic material, electrical, optical, and device aspects. The identity of silicon carbide as a semiconductor for extremely high temperatures is established.

85. Morrison, G. H., Rupp, R. L., and Klecak, G. L.
SPECTROGRAPHIC ANALYSIS OF HIGH-PURITY SILICON
CARBIDE. Analytical Chemistry, Vol. 32, No. 8, pp. 933-
935. 1960.

By using a selective volatilization technique and controlled exposure times dependent on the elements sought, the background due to SiC is greatly reduced and enables small concentrations of impurities in SiC to be determined. The apparatus is the same as reported previously (Rupp, et al, Anal. Abstr., 1961, 8, 595) and an atmosphere of Ar is used.

Impurity elements are determined in the range 0.01 to 10 parts per million. Distillation times, with a 20-ampere dc arc are-for As, Bi, Cd, Ga, Hg, In, Na, P, Pb, Sb, Sn, Tl, and Zn, 6 seconds; for Ag, Al, Be, Ca, Cr, Cu, Ge, and Mn, 25 seconds; for Co, Fe, Mg, Ni, Ti, and V, 60 seconds; for Mo, 15 to 35 seconds; and for Zr, 35 to 50 seconds. Germanium dioxide (10 parts per million) is added as an internal standard for the first two groups, and silicon serves as internal standard for the other groups.

86. Nagy, E. and Weiszburg, J.
ELECTRICAL PROPERTIES OF ELECTROLUMINESCENT SiC CRYSTALS. Acta Phys. Hungar., Vol. 8, No. 1-2, pp. 235-289. 1957. (In German).

The current-voltage characteristic of the specimens was observed to follow the theoretical prediction for the reverse current through an exhaustion barrier modified by the image force correction. It also showed an appropriate temperature variation of the current. Deterioration of the surface at the contact, or prolonged exposure of a crystal to air, produced a conducting layer which could be removed by grinding.

87. N. V. Philips' Gloeilampenfabrieken, Eindhoven, Netherlands.
PROCESS FOR GROWING SEMICONDUCTOR BODIES. Belgian Patent 633,263 issued 5 December 1963. Netherland Application, 6 June 1962.

Semiconductors with p-n junctions, especially of SiC using the process of Lely (Netherlands 87343), are produced by placing on a base of SiC a measured amount of Al_4C_3 . The assembly is heated to 2500° for some hours under Ar. If N_1 is the concentration in atoms per cubic centimeter of semiconductor material of an impurity of the type which determines the type of conduction of the base, N_{11} the corresponding concentrations of the active impurity in the superposed layer, E_1 the sum of the concentrations of all the impurities in the base, and E_2 the sum of all those in the superposed layer, then $E_1N_1 + E_2N_1$ must be $\geq E_1N_{11} + E_2N_{11}$.

88. Namba, M.
OPTICAL PROPERTIES OF SiC IN INFRARED REGION.
Journal of Physical Society of Japan, Vol. 14, No. 2, pp. 228-229. February 1959.

Measurements of reflection and transmission from 2.5 to 16 μ were made on n- and p-type samples about 0.15 millimeter thick. Only the n-type sample, with a resistivity of 100 ohm centimeters, showed free carrier absorption. Both samples had an impurity absorption at 4.3 μ and an intense lattice absorption at 12 μ . The reflection spectrum in the range from 8 to 14 μ indicated that the bonding in the crystal was partly ionic, with values of 5.1 and 7 for the high-frequency and static dielectric constants.

89. National Bureau of Standards, Washington, D. C.
ELECTROLUMINESCENCE AND THERMOELECTRICITY.
Progress Report for Period Ending 1 December 1959. Harman, George G. and Raybold, Richard L. NBS Report No. 6616.
Technical Report No. 1. AFCRC TN 59-999. (AD-229814).

Electroluminescent spectral emission measurements were made on SiC at room temperature and at liquid nitrogen. An energy band diagram was made from these results and a possible type of infrared detector was postulated. A new method of measuring the lifetime of minority carriers in silicon-carbide was tested and produced reasonable results. A thermoelectric measuring apparatus was designed and constructed. It is capable of measuring thermoelectric power from 77°K to 1100°K in air, various ambients, and in moderate vacuum. Tentative results indicate that some high-resistivity n-type SiC changes to p-type at about 500°C and would not be suitable for high-temperature devices. Methods and techniques were developed for the electrodeless plating of Ni and C onto SiC to serve as electrodes. Experimentation with various inter-metallic Ga alloys led to a new technique of bonding thermocouples into samples used in thermopower measurements.

90. North American Philips Company, Inc., New York 17, New York.
SILICON CARBIDE SEMICONDUCTOR DEVICE. Van Daal, Hubert J., Knippenberg, Wilhelmus F., and Huizing, Albert.
U. S. Patent 3,047,439 issued 31 July 1962.

The device comprises an SiC body containing a surface region of n-type conductivity and a fused mass alloyed and adherent to it in ohmic connection thereto, the mass comprising an alloy of gold and 0.1 to 60 percent (at.) of a high-melting-point transition element (molybdenum, tungsten, tantalum, titanium, niobium, vanadium, zirconium, or hafnium).

91. Norton Company, Worchester, Massachusetts.
SILICON CARBIDE CRYSTALS AND PROCESSES AND
FURNACES FOR MAKING THEM. Lowe, Edwin C. U. S.
Patent 3,025,192, issued 13 March 1962.

A crystal of hexagonal silicon carbide for use in electronic equipment is 0.5 to 100 mils thick and has two faces ≤ 0.0625 inch long that are parallel to each other within about 1° , the crystal containing > 1000 parts per million of constituents other than silicon and carbon and having an electrical resistivity of 0.01 to 1000 ohm-centimeter.

92. O'Connor, J. R.
RESEARCH IN THE PREPARATION OF HYPERPURE SINGLE
CRYSTAL SILICON CARBIDE. PB Report 140092. U. S.
Government Research Reports, Vol. 32, No. 1. 1959.

Single crystals of pure SiC obtained to date contain less than 20 parts per million total impurities and may easily be a factor of two or more below this figure. The crystals are quite transparent and are of 10^3 to 10^5 ohm-centimeter resistivity. The mechanisms of purification are examined.

93. O'Connor, J. R. and Smiltens, J.
SILICON CARBIDE - A HIGH TEMPERATURE SEMICONDUCTOR.
Amelinckx, S., and Strumane, G. Paper presented on Surface
Features on Silicon Carbide Crystal Faces, pp. 162-201.
Proceedings of the Conference on Silicon Carbide, Boston,
Massachusetts, 2-3 April 1959. Pergamon Press, 1960.

Silicon carbide crystals have been among the first to be studied in order to demonstrate the role played by dislocations, in the growth of crystals. The remarkable perfection of their faces and the frequent occurrence of high growth shapes make it a particularly attractive material for this type of study. This paper is a review of these observations on industrial silicon carbide.

The remarkable polytypism of silicon carbide finds at least partly its natural explanation in the spiral growth mechanism. Interesting relations exist between the geometry of the growth features and the polytypic structure of the crystals.

Silicon carbide has also been the first substance for which the relation dislocation-etchpit was demonstrated unambiguously. Some more recent work on etching of silicon carbide will be discussed in relation to dislocations in this substance.

94. O'Connor, J. R., and Smiltens, J.
SILICON CARBIDE - A HIGH TEMPERATURE SEMICONDUCTOR. Aukerman, L. W., Gorton, H. C., Willardson, R. K., and Bryson, V. E., Major. Paper presented on Effects of Fast Neutrons on Silicon Carbide, pp. 388-394. Proceedings of the Conference on Silicon Carbide, Boston, Massachusetts, 2-3 April 1959. Pergamon Press, 1960.

Bulk n-type specimens of silicon carbide and silicon carbide junction rectifiers were irradiated with fast neutrons and gamma-rays. Fast neutron irradiation decreased the carrier concentration in bulk specimens. Since the initial carrier concentration was quite large ($n = 9 \times 10^{18}$ cubic centimeter), the percentage change in mobility was greater than the percentage change in carrier concentration. Current-voltage characteristics of the rectifiers were determined before, during, and after irradiation. Up to a total irradiation of 10^{16} fast neutrons per square centimeter, the changes in current-voltage characteristics appear to be due to ionization, that is, essentially no permanent changes were observed. The rate at which the junctions were irradiated was varied from $5 \times 10^9 - 5 \times 10^{11}$ fast neutrons per square centimeter second and from $1.5 \times 10^{10} - 1.5 \times 10^{12}$ photons per square centimeter second. The application of large reverse voltages while in this radiation field tends to increase the resistance and decrease the slope of the reverse characteristic toward an ohmic relationship. This time-dependent effect was not observed either before or after the irradiation in the reactor; nor was it observed during a Co^{60} gamma-irradiation of 10^{11} photons per square centimeter second.

95. O'Connor, J. R., and Smiltens, J.
SILICON CARBIDE - A HIGH TEMPERATURE SEMICONDUCTOR. Bowe, Jeffrey, J., and Frost, Janet A. Paper presented on Shear Seizure Contacts to Silicon Carbide, pp. 423-430. Proceedings of the Conference on Silicon Carbide, Boston, Massachusetts, 2-3 April 1959. Pergamon Press, 1960.

Contacts which can be made to silicon carbide at temperatures not much above room temperature, but which would operate also at high temperatures would be extremely important not only in device fabrication but in the study of silicon carbide phenomena, such as heat-treating.

Shear seizure has been investigated, and techniques for its use in silicon carbide device fabrication have been developed. The resulting contacts have been studied in the light of work function theory.

Techniques have been developed for the application of shear forces on metals to cause seizure between the metals and a semiconducting surface resulting in a union which is very strong mechanically and stable electrically. These may be either ohmic or rectifying in nature. The most successful of the methods for forming the contacts is the use of an appropriately shaped obtuse wedge which converts a small axial force to a radial shear stress. A convenient jig has been designed to hold a wire of 2-mil diameter, to position it and to impart a twisting motion under moderate axial pressure, converting the force to shear stress through the revolving action of inclined microplanes on the surface. Thus far, the contacting has been carried out in air ambient.

As far as has been determined, the shear seizure contact on silicon carbide displays ohmic or rectifying characteristics in accordance with the work function theory of contacts. Low values of resistance, which indicate very good contact between the metal and the semiconductor, are measured.

96. O'Connor, J. R., and Smiltens, J.
SILICON CARBIDE - A HIGH TEMPERATURE SEMICONDUCTOR. Brenner, Walter. Paper presented on A Chemical Approach to the Synthesis of Silicon Carbide, pp. 110-114. Proceedings of the Conference on Silicon Carbide, Boston, Massachusetts, 2-3 April 1959. Pergamon Press, 1960.

The pyrolysis of organosilanes and related compounds offers definite possibilities for the synthesis of silicon carbide. Preliminary experimentation indicates that the decomposition of the organosilicon halides, under suitable processing conditions, can result in the formation of silicon carbide. The decomposition of methyltrichlorosilane in a hydrogen atmosphere in graphite containers is discussed, with emphasis on pertinent characteristics of the reaction products obtained.

97. O'Connor, J. R., and Smiltens, J.
SILICON CARBIDE - A HIGH TEMPERATURE SEMICONDUCTOR. Chang, H. C., Le May, C. Z., and Wallace, L. F. Paper presented on Use of Silicon Carbide in High Temperature Transistors, pp. 496-507. Proceedings of the Conference on Silicon Carbide, Boston, Massachusetts, 2-3 April 1959. Pergamon Press, 1960.

Theoretical analyses of bipolar and unipolar SiC transistors for 500°C operation are presented. Experience with Si and III-V compounds is applied to hexagonal SiC crystals, based on recent data for this compound. Fundamental techniques, such as fusion, diffusion, etching, and ohmic contacts, are studied, with emphasis on the control of junction perfection, depth, and separation.

98. O'Connor, J. R., and Smiltens, J.
SILICON CARBIDE - A HIGH TEMPERATURE SEMICONDUCTOR. Dillon, J. A., Jr. Paper presented on the Interaction of Oxygen with Silicon Carbide Surfaces, pp. 235-240. Proceedings of the Conference on Silicon Carbide, Boston, Massachusetts, 2-3 April 1959. Pergamon Press, 1960.

Studies of the interaction of oxygen with silicon carbide surfaces and the resultant effects on electrical properties are reviewed. Surfaces cleaned in ultra-high vacuum by argon-ion bombardment and 1000°C heating adsorb oxygen at room temperature with a sticking coefficient of the order of 0.01. This adsorption increases the work function by about 0.40 electron volt and decreases the photoelectric yield to about one third the clean-surface value. The adsorbed oxygen can be partially removed by heating in high vacuum at temperatures as low as 500°C, suggesting removal in the form of a volatile oxide. Differences in oxygen adsorption on different crystal faces have been observed which were possibly associated with asymmetry in atomic species on these faces. If samples are heated above 900°C in oxygen ambients of 10^{-1} millimeter of mercury or less, weight losses are observed due to the production of volatile SiO and CO. Oxidation studies carried out at temperatures above 900°C and at pressures of about 1 atmosphere indicate the formation of an SiO₂ layer at the surface. When this layer reaches a certain thickness, it serves as a protective coating which inhibits further oxidation. Exposing the oxidized sample to hydrofluoric acid or heating in the presence of water vapor removes the protective coating and restores the original oxidation rate.

99. O'Connor, J. R., and Smiltens, J.
SILICON CARBIDE - A HIGH TEMPERATURE SEMICONDUCTOR. Ellis, Ray C., Jr. Paper presented on Growth of Silicon Carbide from Solution, pp. 124-129. Proceedings of the Conference on Silicon Carbide, Boston, Massachusetts, 2-3 April 1959. Pergamon Press, 1960.

Silicon carbide crystals have been grown from iron, nickel, and silicon solutions. An excess of silicon in silicon carbide dopes n-type. Only β -SiC was obtained from pure silicon. The α form appears to be impurity stabilized.

100. O'Connor, J. R., and Smiltens, J.
SILICON CARBIDE - A HIGH TEMPERATURE SEMICONDUCTOR. Ellis, Ray C., Jr. Paper presented on Phosphoric Acid and Fused Salt Etching of Silicon Carbide, pp. 420-422. Proceedings of the Conference on Silicon Carbide, Boston, Massachusetts, 2-3 April 1959. Pergamon Press, 1960.

Aqueous phosphoric acid solutions of a density of 1.75 slowly decompose silicon carbide at 215°C to form SiO_2 , CO_2 , H_2 , and CH_4 .

The results of the etching of SiC, Si, C, B, and Ge in a variety of fused salts are discussed.

101. O'Connor, J. R., and Smiltens, J.
SILICON CARBIDE - A HIGH TEMPERATURE SEMICONDUCTOR. Eriksen, W. T. Paper presented on Minority Carrier Lifetime in Silicon Carbide by Carrier Injection Electroluminescence, pp. 376-383. Proceedings of the Conference on Silicon Carbide, Boston, Massachusetts, 2-3 April 1959. Pergamon Press, 1960.

When minority carriers are injected into a semiconductor, recombination may proceed by one or more of several parallel processes. One of these is by radiative recombination with production of photons. The forbidden gap in SiC is large enough so that the radiative transitions give light in the visible spectrum. A square pulse of carriers is injected and the decay of light resulting from the radiative transitions thus induced is measured. If the various modes of recombination are parallel processes, the fastest one is dominant. The light decay typically consists of an initial exponential portion which, at later times, changes into a less rapidly decreasing function of time.

Defining lifetime as the slope of the initial exponential portion of the decay curve, values up to a few tenths of a microsecond have been obtained. The experimental setup to obtain these results is described and some possible interpretations of the decay curves are discussed.

102. O'Connor, J. R., and Smiltens, J.
SILICON CARBIDE - A HIGH TEMPERATURE SEMICONDUCTOR. Faust, J. W., Jr. Paper presented on The Etching of Silicon Carbide, pp. 403-419. Proceedings of the Conference on Silicon Carbide, Boston, Massachusetts, 2-3 April 1959. Pergamon Press, 1960.

Various reasons for etching are reviewed and a brief discussion of the various physical and chemical processes that can be used for etching SiC are given. Experimental evidence is presented to show that the action of boiling phosphoric acid on SiC produces a layer of silicon oxide on the surface. The action of various molten-salt etches on SiC is described. Sodium peroxide causes etching at 350°C. Dislocations are revealed by these etchants for both hexagonal and cubic SiC, and the shapes of the pits are related to edge and screw dislocations. Dislocation densities along intersecting lineage lines indicate a one-to-one correspondence between untruncated pits and dislocations.

103. O'Connor, J. R., and Smiltens, J.
SILICON CARBIDE - A HIGH TEMPERATURE SEMICONDUCTOR. Goffaux, R. Paper presented on Electrical Properties of Silicon Carbide Varistors, pp. 462-468. Proceedings of the Conference on Silicon Carbide, Boston, Massachusetts, 2-3 April 1959. Pergamon Press, 1960.

Silicon carbide varistors and lightning arrestors are made up of granulated SiC generally held together with a suitable binder. Their nonlinear electrical characteristics are interpreted as being due to the presence of barrier layers at the surfaces of the grains of silicon carbide. The surface layers are considered to be made up of a chemically distinct layer (Mott barrier) associated with an electrical junction (Schottky barrier) which becomes predominant at higher voltages. An energy level model for the barrier layer is proposed and the electrical properties of the system are interpreted in terms of this with the additional hypothesis that the electron temperature is a function of the applied electric field and is appreciably higher than the lattice temperature.

We consider first the dc case in which the electron temperature is always at an equilibrium value dependent upon the applied electric field. The free electron density depends upon their temperature and we find for the variation of conductivity σ with applied potential U , a law of the form

$$\sigma = \sigma_0 (1 + \alpha U)^K$$

where α and K are constants depending upon the nature of the medium. In particular K is essentially given by the ratio of the donor activation energy to the Debye characteristic energy of the lattice. For potentials for which $\alpha U \gg 1$, the relation reduces to $\sigma = BU^K$, the well-known empirical expression for varistors.

The estimated values of K are in good agreement with the experimental values.

The varistor characteristic when an alternating potential is applied is interpreted in terms of an equivalent circuit composed of a resistor and a capacitor, both of which are voltage dependent, in parallel. The capacity is calculated as that of a Schottky barrier in which the density of ionized donors depends on the applied field.

When a varistor is subjected to pulses of very short duration, the V - I curve develops a hysteresis loop. The characteristic has also been interpreted on our model. The dependence of initial slope upon the steepness of the leading edge of the applied pulse is due to the finite value of the time constant for the establishment of an electron avalanche, while the hysteresis is due to delayed recombination arising from trapping. Good agreement with the experimental results of Busch and Teszner are obtained.

104. O'Connor, J. R., and Smiltens, J.
SILICON CARBIDE - A HIGH TEMPERATURE SEMICONDUCTOR. Goldberg, Colman, and Ostroski, John W. Paper presented on Silicon Carbide Rectifiers, pp. 453-461. Proceedings of the Conference on Silicon Carbide, Boston, Massachusetts, 2-3 April 1959. Pergamon Press, 1960.

Rectifiers capable of 500°C operation have been made from silicon carbide. The crystals are grown in a Lely-type furnace and contain junctions grown by alternately doping with aluminum and nitrogen. Processing of the crystals and rectifier fabrication, encapsulation, and characteristics will be discussed.

105. O'Connor, J. R., and Smiltens, J.
SILICON CARBIDE - A HIGH TEMPERATURE SEMICONDUCTOR. Halden, F. A. Paper presented on Growth of Silicon Carbide Crystals from solution in Molten Metal Alloys, pp. 115-123. Proceedings of the Conference on Silicon Carbide, Boston, Massachusetts, 2-3 April 1959. Pergamon Press, 1960.

Small β -silicon carbide crystals have been grown from metal alloy melts. The method consists, essentially, of admitting a silicon carbide seed into a silicon-rich melt which is supersaturated with carbon by means of a three-dimensional temperature gradient. Crystals grown from silicon melts are transparent, yellow in color, and appear to have impurity concentrations in the range of 10^{-3} atom percent, while those grown from iron-silicon alloys are transparent, blue to green in color, and contain about 0.4 percent iron. Crystals thus far produced are small and badly stressed. They tend to grow in polycrystalline agglomerates which are easily separated into small crystals, many of which appear to be single. Single crystals needles approximately 0.5 millimeter in diameter by 4 millimeters long, and platelets about 0.5 millimeter thick by 8 millimeter across, have been grown. Initial studies have provided considerable insight into the thermal conditions required for crystal growth by this method. Work is being continued to determine optimum crystal growth requirements as well as the influence of melt composition on growth and electrical properties.

106. O'Connor, J. R., and Smiltens, J.
SILICON CARBIDE - A HIGH TEMPERATURE SEMICONDUCTOR. Hamilton, D. R. Paper presented on Preparation and Properties of Pure Silicon Carbide, pp. 43-52. Proceedings of the Conference on Silicon Carbide, Boston, Massachusetts, 2-3 April 1959. Pergamon Press, 1960.

Extensive experiments have been carried out on the preparation of single crystals of SiC in a graphite tube furnace, after the method of Lely. A wide range of ambients have been employed. Crystals have been grown in argon, hydrogen, and over a wide

range of temperatures. Emphasis is laid upon the relationship between these variables and the composition and habit of the material grown.

107. O'Connor, J. R., and Smiltens, J.
SILICON CARBIDE - A HIGH TEMPERATURE SEMICONDUCTOR. Hergenrother, K. M., Mayer, S. E., and Mlavsky, A. I. Paper presented on Epitaxial and Single Crystal Growth onto Silicon Carbide Seeds, pp. 60-66. Proceedings of the Conference on Silicon Carbide, Boston, Massachusetts, 2-3 April 1959. Pergamon Press, 1960.

Studies of the theoretical aspects of crystal growth from the vapor phase, particularly with respect to factors which prevent secondary nucleation during growth onto a seed, are reported. The theory is applied to the problem of growing single-crystal SiC from the vapor phase epitaxially onto seeds. A furnace, designed to meet the limiting parameters, has been used to grow layers of high-purity SiC onto seeds. The electrical and physical properties of films prepared in this manner, which are dependent on various growing parameters as well as the purity of the starting materials, are discussed. Single crystals of the cubic modification several cubic millimeters in volume have been grown in the furnace by random nucleation. Methods of growing larger cubic crystals onto cubic as well as onto hexagonal seeds are described. The properties of junctions made by epitaxial deposition films are also presented.

108. O'Connor, J. R., and Smiltens, J.
SILICON CARBIDE - A HIGH TEMPERATURE SEMICONDUCTOR. Hopkins, Albert L., Jr. Paper presented on The Analysis of Diode Switching Networks Employing Point Contact Silicon Carbide Diodes, pp. 482-495. Proceedings of the Conference on Silicon Carbide, Boston, Massachusetts, 2-3 April 1959. Pergamon Press, 1960.

It is relatively easy to analyze and design digital diode gates, or switching networks, when the diodes have nearly ideal voltage-current characteristics. When the diodes have only moderately nonlinear and asymmetric characteristics, however, the task is greatly complicated.

Silicon carbide diodes have the advantage of being fairly insensitive to environmental changes. Thus far, however, it has proven quite difficult to obtain nearly ideal characteristics, whereas diodes of moderate quality are readily obtainable.

The paper treats diode switching networks composed of nonideal diodes. An analytic method is presented which is based on the calculation of a two-parameter family of functions describing the behavior of a one-level diode switch. Using this family of functions, one can design and analyse a two-level switching network, taking into account the loading imposed by the second level on the first level and the effects of variations in diode characteristics.

This method is used to design and analyze two-level switching networks composed of point contact silicon carbide diodes. The merit of a network for any particular application can be deduced from a graphical representation of its amplitude discrimination as a function of the numbers of inputs to each level.

109. O'Connor, J. R., and Smiltens, J.
SILICON CARBIDE - A HIGH TEMPERATURE SEMICONDUCTOR. Jagodzinski, H., and Arnold, H. Paper presented on Anomalous Silicon Carbide Structures, pp. 136-146. Proceedings of the Conference on Silicon Carbide, Boston, Massachusetts, 2-3 April 1959. Pergamon Press, 1960.

According to the results of structure determination of SiC, the general structural principles of all modifications are very similar. They may be regarded as an ordered stacking sequence of hexagonal SiC layers, each of which is capable of three positions, corresponding to the well-known stacking sequence of close-packed arrangements. Each structure is characterized by a certain number of layers, forming the identity period of its structure. On account of the tetrahedral arrangement of nearest neighbors, the distance Si-C seems to be the same for all different modifications. This is checked by the strict coincidence of certain reflections in X-ray powder photographs of high accuracy.

110. O'Connor, J. R., and Smiltens, J.
SILICON CARBIDE - A HIGH TEMPERATURE SEMICONDUCTOR. Jorgensen, Paul J., Wadsworth, Milton E., and Cutler, Ivan B. Paper presented on The Kinetics of the Oxidation of Silicon Carbide, pp. 241-250. Proceedings of the Conference on Silicon Carbide, Boston, Massachusetts, 2-3 April 1959. Pergamon Press, 1960.

The rate of oxidation of silicon carbide was measured in an atmosphere of dry oxygen between the temperatures of 900° and 1600°C. The rate was studied by using a thermogravimetric apparatus and was found to be diffusion controlled. The products of oxidation are amorphous silica or cristobalite, depending on the temperature.

The effect of surface area was determined and a correlation between the various sizes was made with the aid of an equation derived upon the assumptions that the reaction was (1) diffusion controlled, (2) the particles were essentially spherical, and (3) the surface area was constantly changing.

The derived equation is

$$[1 - (1 - R)^{1/3}]^2 = \frac{2\lambda_0^2}{r_0^2} k't$$

where R is the fraction of the reaction completed, k' is the specific rate constant, t is time, r is the average initial particle size, and λ is the mean diameter of a molecule.

The effect of changing the impurities within the silicon carbide from 99 percent pure to < 320 parts per million impurity did not affect the rate of oxidation. However, the effects of water vapor pressure and the partial pressure of oxygen were found to be extremely critical.

111. O'Connor, J. R., and Smiltens, J.
SILICON CARBIDE - A HIGH TEMPERATURE SEMICONDUCTOR. Kendall, James T. Paper presented on Growing of Silicon Carbide Crystals By Gaseous Cracking, pp. 67-72. Proceedings of the Conference on Silicon Carbide, Boston, Massachusetts, 2-3 April 1959. Pergamon Press, 1960.

A general discussion is given of the factors involved in the growth of large silicon carbide single crystals by the thermal decomposition of a volatile substance such as CH_3SiCl_3 or a mixture of substances such as SiCl_4 plus a hydrocarbon. The factors considered are presence of hydrogen as a carrier gas, temperature and nature of the substrate, pressure, concentration of the reactants, and presence of impurities. Some experimental results are presented.

112. O'Connor, J. R., and Smiltens, J.
SILICON CARBIDE - A HIGH TEMPERATURE SEMICONDUCTOR. Lipson, H. G. Paper presented on Infrared Transmission of Alpha Silicon Carbide, pp. 371-375. Proceedings of the Conference on Silicon Carbide, Boston, Massachusetts, 2-3 April 1959. Pergamon Press, 1960.

Infrared transmission measurements from 1 to 25 μ have been made on clear hexagonal SiC samples obtained from several sources. All samples show the broad fundamental band in the vicinity of 12 μ and several weaker lattice absorption bands in the 4 to 10 μ region. Measurements indicate that the transmission of clear SiC is limited principally by reflection loss and these lattice absorption bands, except at the longer wavelengths where weak absorption is noted for some samples. The transmission of clear SiC is compared with that of green SiC containing nitrogen as an impurity and with that measured by other investigators.

113. O'Connor, J. R., and Smiltens, J.
SILICON CARBIDE - A HIGH TEMPERATURE SEMICONDUCTOR. Lowe, Lester F., Thompson, Harriet D., and Cali, J. Paul. Paper presented on Neutron Activation Analysis of Silicon Carbide, pp. 221-226. Proceedings of the Conference on Silicon Carbide, Boston, Massachusetts, 2-3 April 1959. Pergamon Press, 1960.

Silicon carbide was analyzed by means of neutron activation for seven elements: Ni, Mn, Cu, Zn, Sb, Mo, and Fe. This method is several orders of magnitude more sensitive than the spectrographic method for many elements.

After irradiation with thermal neutrons at the reactor at Brookhaven National Laboratory, the sample was decomposed at 1250°C with chlorine and oxygen. The induced impurity activities were separated from each other and then counted by means of a Geiger counter to determine their impurity levels. The results were in agreement with the spectrographic data available. Although only seven elements were checked, there is no reason why the method could not be extended to many others.

114. O'Connor, J. R., and Smiltens, J.
SILICON CARBIDE - A HIGH TEMPERATURE SEMICONDUCTOR. Merz, Kenneth M. Paper presented on Crystal, Whisker, and Microcrystalline Forms of Silicon Carbide, pp. 73-83. Proceedings of the Conference on Silicon Carbide, Boston, Massachusetts, 2-3 April 1959. Pergamon Press, 1960.

The preparation and some of the properties of β -SiC crystals grown from gaseous reactants and silicon melts are described. A description of the recently discovered 2H polytype of alpha SiC (wurtzite structure) is given together with details of the preparation of this material from methyl trichlorosilane at 1400° to 1500°C. The synthesis of α -SiC whiskers of about 5 μ diameter and 1 centimeter length at 1450°C is given. A microcrystalline dense SiC with a particle size of about 500 Å is described. The problem of the stability relationship of α and β -SiC is considered in the light of the preparation of α -SiC at much lower temperatures than previously reported.

115. O'Connor, J. R., and Smiltens, J.
SILICON CARBIDE - A HIGH TEMPERATURE SEMICONDUCTOR. Minamoto, M. T. Paper presented on Thermocouple Furnace for Device Fabrication, pp. 443-446. Proceedings of the Conference on Silicon Carbide, Boston, Massachusetts, 2-3 April 1959. Pergamon Press, 1960.

A furnace for the fabrication of silicon carbide devices is described. The furnace consists primarily of a graphite crucible supported by a polycrystalline SiC rod, commercially available as heating elements. The interface of the crucible base and the support rod form the hot junction of a thermocouple, which measures directly the temperature at the base of the crucible. The thermocouple (C-SiC) produces an electromotive force of approximately 300 volt per degree C which is essentially linear and stable up to 1800°C. Details of the furnace, including the preparation of the junction and methods of thermal and electrical insulation, are given.

116. O'Connor, J. R., and Smiltens, J.
SILICON CARBIDE - A HIGH TEMPERATURE SEMICONDUCTOR. Morrison, George H., and Rupp, Richard L. Paper presented on Analysis of Impurities in Silicon Carbide, pp. 227-234. Proceedings of the Conference on Silicon Carbide, Boston, Massachusetts, 2-3 April 1959. Pergamon Press, 1960.

As in the case of other semiconductor materials, the need for extremely sensitive methods of analysis of trace impurities in silicon carbide is essential to the development of methods of ultrapurification, as well as to a better understanding of the role of impurities on the electrical characteristics of the material.

A review is presented of the various techniques of trace analysis that are applicable to the determination of impurities in silicon carbide and other semiconductor materials, and the advantages and limitations of these methods are given.

In connection with an AFCRC contract for the development of a sensitive and convenient method for the analysis of impurities in silicon carbide, results to date are presented on an emission spectrographic method of enhanced sensitivity. The method is based on the selective volatilization of impurities from the silicon carbide matrix. Preparation of spectrographic standards is described and the present limits of sensitivity are presented.

117. O'Connor, J. R., and Smiltens, J.
SILICON CARBIDE - A HIGH TEMPERATURE SEMICONDUCTOR. Pohl, Robert G. Paper presented on Electrical Properties of Beta Silicon Carbide, pp. 312-330. Proceedings of the Conference on Silicon Carbide, Boston, Massachusetts, 2-3 April 1959. Pergamon Press, 1960.

Using micromanipulator techniques, electrical measurements on pure and impure single crystals and on aggregates of beta SiC indicate an electron mobility $\mu_e = 32$ square centimeters per volt-second, a thermal energy gap $E_{GAP} = 1.90 \pm 0.10$ electron volt, and a thermoelectric power $Q = -105$ microvolt per degree. Impure dark blue crystals were n type with resistivity $\rho = 10^{-3} \Omega$ -centimeter and 2×10^{19} impurities per cubic centimeter. Light yellow crystals had resistivities $\rho = 1-100 \Omega$ -centimeter and $10^{17}-10^{15}$ impurities per cubic centimeter. Comparison of optical absorption versus photon energy and electrical conductivity versus temperature data suggests an experimental confirmation of a valley-type band model for alpha and beta SiC.

118. O'Connor, J. R., and Smiltens, J.
SILICON CARBIDE - A HIGH TEMPERATURE SEMICONDUCTOR. Primak, William. Paper presented on Anisotropy of the Radiation-Induced Expansions of Silicon Carbide, pp. 385-387. Proceedings of the Conference on Silicon Carbide, Boston, Massachusetts, 2-3 April 1959. Pergamon Press, 1960.

Seven tabular fragments of hexagonal (presumably α -) silicon carbide were ground into a shape suitable for Fizeau interferometer measurements, in which their lengths were compared with similar vitreous silica posts. Three of these were irradiated in a nuclear reactor for about 1.08×10^{20} damaging neutrons per square centimeter, three for about 1.80×10^{20} , and one was retained as a standard. They were measured again after the irradiations and their densities were also determined. From these data the fractional expansions along the optic axis and perpendicular to it were calculated and were found to be in the ratio 0.97 for both irradiations.

119. O'Connor, J. R., and Smiltens, J.
SILICON CARBIDE - A HIGH TEMPERATURE SEMICONDUCTOR. Rudenberg, H. Gunther. Paper presented on The Derivation of Material Properties From Measurements on pn Junctions, pp. 447-452. Proceedings of the Conference on Silicon Carbide, Boston, Massachusetts, 2-3 April 1959. Pergamon Press, 1960.

This paper presents some of the methods utilized in silicon carbide, silicon, and germanium research for providing information on the material properties in the vicinity of pn junctions. Available junction theories use known material parameters to predict junction characteristics, and this paper examines those theories that can provide information for the evaluation of the material parameters. An advantage of the method is its application to small samples, as microjunctions may readily be made. Additional information may be obtained from the temperature behavior of the junction characteristics. The static voltage-current characteristic of a junction provides only little useful information, namely the forward spreading resistance in devices not subject to conductivity modulation, and the inverse avalanche voltage from clean devices. Junction pulse recovery time provides the order of magnitude of minority carrier lifetime. Most useful is the capacitance-voltage curve of a pn junction, as the space-charge widening as a function of voltage gives direct information on the impurity concentrations and gradients at the junctions. This will

be applied to diffused as well as to linear-graded or uniformly-doped junctions. Here the space charge layer acts as a variable width microprobe, controlled by the applied voltage. This method has also been applied to the determination of diffusion constants. These methods are surveyed, and the capacitance-voltage method illustrated by sample evaluations from silicon carbide and silicon junctions.

120. O'Connor, J. R., and Smiltens, J.
SILICON CARBIDE - A HIGH TEMPERATURE SEMICONDUCTOR. Scace, R. I., and Slack, G. A. Paper presented on the SiC and GeC Phase Diagrams, pp. 24-30. Proceedings of the Conference on Silicon Carbide, Boston, Massachusetts, 2-3 April 1959. Pergamon Press, 1960.

The solubility of carbon in silicon has been measured over the temperature range 1408° to 2900°C. The enthalpy of solution is 59 ± 3 kcal/mol. A phase diagram for the system SiC is presented, embodying these solubility data as well as the results of other high-temperature experiments with silicon carbide. It is found that SiC possesses a peritectic point at $2830^\circ \pm 40^\circ\text{C}$. These studies were carried out in argon at pressures as high as 35 atmosphere. Solubilities of carbon in germanium were measured in the temperature range 2780° to 3170°C, at argon pressures up to 55 atmosphere.

121. O'Connor, J. R., and Smiltens, J.
SILICON CARBIDE - A HIGH TEMPERATURE SEMICONDUCTOR. Smith, Allen H. Paper presented on Formation of SiC From the Vapors, pp. 53-59. Proceedings of the Conference on Silicon Carbide, Boston, Massachusetts, 2-3 April 1959. Pergamon Press, 1960.

Methods of channeling the vapors of SiC to form crystals in a predetermined manner are discussed. The methods have three common points: (1) only silicon and carbon are used in the high-temperature zone; (2) flow of silicon and carbon vapors in an arbitrary direction is controlled by temperature gradient; and (3) pyrolytic graphite, impervious to silicon vapor, is used as a container or funneling device. The methods employed permit use of highest purity materials and avoid the contamination inherent in massive furnaces with carbon black insulation.

122. O'Connor, J. R., and Smiltens, J.
SILICON CARBIDE - A HIGH TEMPERATURE SEMICONDUCTOR. Spitzer, W. G., Kleinman, D. A., Frosch, C. J., and Walsh, D. J. Paper presented on Infrared Properties of Silicon Carbide, pp. 347-365. Proceedings of the Conference on Silicon Carbide, Boston, Massachusetts, 2-3 April 1959. Pergamon Press, 1960.

Infrared transmission and reflectivity measurements from 1 to 25 microns have been made on several samples of green alpha (hexagonal) SiC. The residual ray bands have been observed for the ordinary and extraordinary rays. The resonance frequencies are $2.380 \times 10^{13} \text{ sec}^{-1}$ (1260 μ) and $2.356 \times 10^{13} \text{ sec}^{-1}$ (12.73 μ), respectively. From the reflectivity, the high frequency dielectric constant is found to be 6.7. A careful analysis shows that the residual ray bands can be fitted within experimental error by the classical dispersion theory with the correct choice of the dispersion parameters. From the parameters, the value 10.0 is obtained for the low-frequency dielectric constant. The effective charge is 0.94e. Complete description of the residual ray band for the ordinary ray required, in addition to the main resonance, a weak resonance at $2.647 \times 10^{13} \text{ sec}^{-1}$ (11.33 μ). A study on the effects of several different surface treatments shows the reflectivities reported here are an intrinsic property of the crystal. The room temperature absorption coefficient as a function of wavelength in the range 1 to 10 μ has been determined from transmission measurements. A number of weak lattice bands are observed between 5 and 10 μ .

Films of cubic silicon carbide have been grown by the reaction of methane with a high purity silicon surface at 1300°C. Windows of SiC were produced by etching away portions of the silicon. Transmission and reflection measurements in the range 1 to 15 μ have been carefully analyzed according to classical dispersion theory. The dispersion parameters have been determined for the fundamental resonance at 12.60 μ . The dispersion parameters are essentially the same as those for the ordinary ray in the hexagonal α -II form.

123. O'Connor, J. R., and Smiltens, J.
SILICON CARBIDE - A HIGH TEMPERATURE SEMICONDUCTOR. Straughan, Virgil E., and Mayer, Edward F. Paper presented on Growth of β -Silicon Carbide Crystals by Gaseous Cracking, pp. 84-93. Proceedings of the Conference on Silicon Carbide, Boston Massachusetts, 2-3 April 1959. Pergamon Press, 1960.

A technique is described for the preparation of relatively large crystals of β -silicon carbide. A mixture of methyltrichlorosilane and toluene was transported into a heated reactor by hydrogen carrier gas where pyrolysis occurred. Formation of silicon carbide followed where it deposited on a hot substrate to produce crystals. A unique feature of the reactor is its ability to maintain more nearly optimum crystal growth conditions for an extended period. This feature has contributed to the growth of β -silicon carbide crystals up to 2 millimeters in diameter. A comparison is made of the purity of crystals resulting from this investigation and those made commercially and by sublimation.

124. O'Connor, J. R., and Smiltens, J.
SILICON CARBIDE - A HIGH TEMPERATURE SEMICONDUCTOR. Susman, Sherman, Spriggs, R. Spencer, and Weber, Harold S. Paper presented on The Vapor Phase Growth of β -Silicon Carbide Single Crystals, pp. 94-109. Proceedings of the Conference on Silicon Carbide, Boston, Massachusetts, 2-3 April 1959. Pergamon Press, 1960.

A technique is presented for growing β -SiC single crystals from the vapor phase. The flow system and reaction chamber for the silicon and carbon carrying components are described. The results obtained with (1) mixtures of silicon tetrachloride and toluene, (2) methylchlorosilanes, and (3) toluene and elemental silicon are presented. The crystals grown by this method range from small, light yellow polyhedra (10 micron in breadth) to thin whiskers (20 micron in breadth and 5 millimeters long) and to larger ellipsoidal crystals. These single crystals are approximately 1 millimeter long, 0.2 millimeter in breadth, light yellow-green in color, and completely transparent when viewed along their growth axis. The results are discussed in terms of current concepts of crystal growth.

125. O'Connor, J. R., and Smiltens, J.
SILICON CARBIDE - A HIGH TEMPERATURE SEMICONDUCTOR. Taylor, A., and Jones, R. M. Paper presented on The Crystal Structure and Thermal Expansion of Cubic and Hexagonal Silicon Carbide, pp. 147-154. Proceedings of the Conference on Silicon Carbide, Boston, Massachusetts, 2-3 April 1959. Pergamon Press, 1960.

Silicon carbide exists in several allotropic modifications, one of which is cubic, the remainder being hexagonal. However, they are all variants of a simple motif, being based upon a tetrahedral grouping of silicon and carbon atoms. The thermal expansions of cubic β -SiC and hexagonal Mod II have been studied by X-ray diffraction techniques over the temperature range -190° to 1200°C .

The hexagonal unit cell of SiC Mod II at room temperature has lattice parameters $a = 3.0806_5$, $c = 15.1173_8 \text{ \AA}$. The ideal axial ratio c/a , based on the stacking of perfect tetrahedral units would be 3×1.632 , but in fact is 3×1.6357 . Lattice parameter determinations show an increase in c and a with rising temperature, the axial ratio increasing from 4.907 at -190°C to 4.908 at 750°C , falling again to 4.907 at 1200°C . The coefficient of thermal expansion of the cubic form, which bears an interesting analogy to that of diamond, is roughly in accord with the Grüneisen law and lies intermediate between the expansion coefficients for the c and a directions of the hexagonal form. It rises from zero at $T = -273^{\circ}\text{C}$ to 4.5×10^{-6} at 300° and then shows a further sharp increase in the region of 700°C , rising slowly to 5.4×10^{-6} at 1200°C .

126. O'Connor, J. R., and Smiltens, J.
 SILICON CARBIDE - A HIGH TEMPERATURE SEMICONDUCTOR. Taylor, Theodore C. Paper presented on Fused Contacts to Silicon Carbide, pp. 431-442. Proceedings of the Conference on Silicon Carbide, Boston, Massachusetts, 2-3 April 1959. Pergamon Press, 1960.

Experimental studies are reported for some fused rectifying and nonrectifying contacts to silicon carbide. Silicon which is heavily doped with arsenic or phosphorus is shown to give essentially nonrectifying contacts to n-type silicon carbide crystals when alloyed at temperatures near 1500°C . The measured behavior of these contacts includes the effects of some spreading resistance in the silicon carbide. It is therefore not known whether the contact impedance alone is nonrectifying, or alternatively, negligible compared to the spreading resistance.

The development of a rectifying structure is reported, wherein pure aluminum is fused to n-type silicon carbide, giving a layer of aluminum carbide between the aluminum and the silicon carbide crystal. Electrical measurements show that the rectifying barrier in this structure is at or near the

aluminum carbide-silicon carbide interface. This type of rectifier is shown to have room temperature electrical characteristics similar to those reported elsewhere for aluminum-doped fused junctions in silicon carbide. The electrical characteristics at elevated temperature are less promising than those of silicon carbide junctions, although some rectification persists at 400°C.

127. O'Connor, J. R., and Smiltens, J.
SILICON CARBIDE - A HIGH TEMPERATURE SEMICONDUCTOR. Verma, A. R. Paper presented on Polytypism and Surface Structure of Silicon Carbide Crystals-Interferometric and X-Ray Studies, pp. 202-216. Proceedings of the Conference on Silicon Carbide, Boston, Massachusetts, 2-3 April 1959. Pergamon Press, 1960.

Studies of the surface structure of a number of SiC crystals of different polytypes, by a combination of phase-contrast microscopy and multiple-beam interferometry, are reported. The structure of different polytypes has been determined by X-ray diffraction methods. A correlation between the spiral step-heights and X-ray unit cells has helped to explain the origin of polytypism in SiC crystals in terms of the dislocation theory. A mixture of polytypes and their variation on a microscopic scale is reported, and a variety of observations on SiC surfaces, some of which are still to be explained, is noted.

128. Pasyukov, V. V., Kholuyanov, G. F., and Chirkin, L. K.
CONCERNING THE DYNAMIC CURRENT-VOLTAGE CHARACTERISTICS OF SILICON CARBIDE RESISTORS. Soviet Physics-Solid State, Vol. 2, pp. 403-405. September 1960. (A translation).

The dynamic current-voltage curves of low-voltage nonlinear silicon carbide resistors at low-current densities are discussed. These curves differ essentially from the dynamic current-voltage characteristics of resistors operating under the conditions of Vilit arresters. The hysteresis of the current-voltage curves is due to the process of charging and discharging of the capacity of a nonlinear resistor and is not connected with microheating of contacts between silicon carbide crystals. The capacitance of nonlinear resistors made of green and black silicon carbide is independent of the frequency in the range 50 kilocycles to 25 megacycles and of the dc bias voltage.

129. Patrick, L.
STRUCTURE AND CHARACTERISTICS OF SILICON CARBIDE
LIGHT-EMITTING JUNCTIONS. Journal of Applied Physics,
Vol. 28, No. 7, pp. 765-776. July 1957.

Current-voltage characteristics of SiC p-n junctions were measured on light-emitting samples prepared in such a way as to minimize leakage at the periphery and through blue spots. The characteristics of such junctions are found to be very different from those previously reported. From the characteristics it is deduced that these junctions have a p-n*-n structure rather than a p-n structure. The high resistivity n* layer is essential for the observed light-emission. This layer, together with the blue spots which short circuit the p-n* junction, determines the form of the reverse characteristic. Two portions of the reverse characteristic take their form from space-charge-limited currents in the n* layer. A theory is given of the forward characteristic of the p-n*-n structure and compared with the experimental current-voltage curve. The theory permits one to obtain a value of the thermal energy gap from a forward characteristic at a single temperature. From a fit of this data the energy gap is found to be 2.83 ± 0.1 electron volt at room temperature. Results of some experiments on crystal growing are presented and an explanation of the manner of growth of light-emitting junctions is suggested.

130. Patrick, L. and Choyke, W. J.
IMPURITY BANDS AND ELECTROLUMINESCENCE IN SiC
P-N JUNCTIONS. Journal of Applied Physics, Vol. 30, No. 2,
pp. 236-248. February 1959.

A study of the electroluminescence of certain SiC p-n junctions, between 77°K and 830°K, and over a range of 10^4 in current density, has been used to verify and to extend a 3-part model (p-n*-n) of the junctions derived from electrical measurements. The electroluminescence, due to recombination in n*, consists of two parts, which may be called impurity luminescence and intrinsic recombination radiation. At low temperatures ($\leq 200^\circ\text{K}$) only the former is present. Several effects of impurity banding on the electroluminescence can be predicted, and some of these have now been observed. The most striking of these effects is the Fermi-level emission edge in the low-temperature spectra, an edge which moves to higher energies with increasing current density because of the impurity band injection

of electrons. The predominance of impurity band injection at low temperatures excludes the possibility of intrinsic recombination radiation. At high temperatures, however, electron injection is by way of the conduction band. The intrinsic recombination radiation observed at higher temperatures has been compared with that calculated from earlier absorption data, using the theory of van Roosbroeck and Shockley. From the comparison, the density of electrons in the conduction band and the electron lifetime (10^{-8} second) at room temperature are obtained. This lifetime is very short compared with the measured hole lifetime, and is possibly a result of the merging of impurity band and conduction band levels. This junction model is now detailed enough to estimate impurity level densities and the hole and electron densities. From these, one is able to calculate cross sections for the various recombination processes involved. All luminescent processes have been found to have a recombination cross section of approximately 10^{-23} square centimeter.

131. Patrick, L.
POLARIZATION OF THE LUMINESCENCE OF DONOR-ACCEPTOR PAIRS. Physical Review, Vol. 117, No. 6, pp. 1439-1441. 15 March 1960.

The polarization is calculated for donor-acceptor pair luminescence in SiC. Certain degrees of polarization depend only on the axial directions of the donor-acceptor pairs, thus permitting one to identify emission by such centers in SiC, or in other uniaxial crystals with tetrahedral bonds. A comparison with experiment is inconclusive because of insufficient resolution. The Prener-Williams conclusion about nearest-neighbor donor-acceptor pairs are discussed.

132. Patrick, L., Hamilton, D. R., and Choyke, W. J.
OPTICAL PROPERTIES OF 15R SiC: LUMINESCENCE OF NITROGEN-EXCITON COMPLEXES, AND INTERBAND ABSORPTION. Physical Review, Vol. 132, pp. 2023-2031. 1 December 1963.

Optical experiments on 15R SiC are reported, and the results are compared with those given earlier for 6H SiC. The adsorption edge is due to indirect, exciton-producing transitions, across an exciton energy gap of 2.986 electron volts at 6°K. Two distinct photoluminescence spectra are found, due to two kinds of nitrogen-exciton complexes. These spectra

consist of series of lines, from which 18 phonon energies are obtained. Only four series of lines are observed in each spectrum, although there are five inequivalent nitrogen sites in 15R SiC. The four nitrogen donor ionization energies are found to be approximately 0.14, 0.16, and 0.20 electron volt. These, and other binding energies, are somewhat smaller than in 6H SiC. As in the 6H SiC data, there was evidence of exciton hopping, of localized vibrations, of the presence of six conduction band minima, and of a second valence band, split off 4.8 million electron volts by spin-orbit interaction.

133. Philipp, H. R.
INTRINSIC OPTICAL ABSORPTION IN SINGLE-CRYSTAL SILICON CARBIDE. Physical Review, Vol. 111, No. 2, pp. 440-441. 15 July 1958.

The optical absorption of single-crystal silicon carbide was measured in both the cubic and hexagonal, type 6H, modification. The curves nearly coincide for absorption coefficients above 10^3 centimeter⁻¹. At longer wavelengths, the cubic structure absorbs more strongly. The absorption coefficient is 100 centimeters⁻¹ at 2.62 and 3.12 electron volts, respectively, in these two crystals. The electron affinity of silicon carbide is estimated from photoelectric data to be about 4 electron volts.

134. Poch, W. and Dietzel, A.
FORMATION OF SILICON CARBIDE FROM SILICA AND CARBON. Berichte der Deutschen Keramischen Gesellschaft, Vol. 39, No. 8, pp. 413-426. 1962. (In German).

The SiC-O equilibrium diagram drawn by calculation from the thermodynamic data for SiO₂, SiO (gas), Si, SiC, and C (graphite) was used to design some of the reaction experiments under various conditions of temperature and pressure of CO and SiO. Quantitative chemical and X-ray analyses were made on the various reactions at temperatures up to 2500°C. The mechanisms of the reactions are discussed.

135. Pohl, Robert G.
PURE SILICON CARBIDE IN SINGLE CRYSTAL FORM-LITERATURE SURVEY ON SILICON CARBIDE. PB Report 139338. U. S. Government Research Reports, Vol. 32, No. 5, pp. 629-630. 1959.

Pyrolytic decomposition of silanes and of silicon tetrachloride and hydrocarbons was carried out in a high-temperature vapor phase reaction. Constructional features of an electric high-temperature reaction furnace are given. The growth rate for high-purity single crystals of β -SiC of preferred crystalline growth habits is quite small, 0.1 millimeter per hour or less. The best crystals were light yellow, 1 to 2 millimeters long, and 0.2 millimeter in diameter. Electrical measurements on pure and impure single crystals and on aggregates of β -SiC indicate an electron mobility $\mu_{e^-} = 32$ square centimeters per volt second, a thermal energy gap $E_{\text{gap}} = 1.90 \pm 10$ electron volts, and a thermoelectric power $Q = -105$ microvolt per degree. A literature survey, with abstracts, of 227 references is included.

136. Porozhnikova, G. and Kholuyanov, G.
PHOTOCONDUCTIVITY OF MODIFIED SILICON CARBIDE.
Fizika Tverdogo Tela, pp. 3657-3622. December 1961.
(In Russian).

No abstract.

137. Raytheon Manufacturing Co., Waltham, Massachusetts.
BETA SILICON CARBIDE. Scientific Report No. 1, S-147.
Warschauer, D. M. 25 April 1960. AFCRC TN 60-555.
(AD-238179). Contract AF 19(604)-6133.

The purpose of this contract is to grow large, perfect crystals of beta silicon carbide of as high purity as possible, to investigate methods of growing crystals having controlled impurity content, including production of junctions, and to measure the important electrical properties of the material produced. The results of tests for the optimum composition of gas for the vapor-decomposition method of growth indicate that best results are achieved when hydrogen and silicon tetrachloride are used alone, rather than with addition of a carbon-bearing compound. The best crystals have been grown at 1950°C ; these crystals are stoichiometric to within 0.3 percent, and the impurity content does not exceed 0.003 percent of the impurity most abundant. It has been demonstrated that formation of methane and of high-molecular weight complexes of silicon dichloride are important factors in the growth process. Somewhat smaller crystals of a different shape are being grown by deposition from solution; advances have been made in improving the purity of this material, and preliminary

measurements of electrical properties are under way. Work not performed under the contract but related to it includes measurement of the optical absorption edge in cubic silicon carbide as a function of temperature. The first of these measurements has been made. Work in this area and on the growth and electrical properties is expected to continue.

138. Raytheon Manufacturing Co., Waltham, Massachusetts.
BETA SILICON CARBIDE. Scientific Report No. 2.
Warschauer, D. M. 15 September 1960. AFCRL TN 60-1103.
(AD-244795L). Contract AF 19(604)-6133.

No automatic release to Foreign Nationals.

This report includes:
FORMATION OF SILICON CARBIDE IN SILICON SOLUTION,
by A. Smith, 11 August 1960, (Technical Memorandum No. T-237).

PREPARATION OF CUBIC SILICON CARBIDE BY GASEOUS CRACKING, by Ray C. Ellis, Jr. 31 August 1960, (Technical Memorandum No. T-240).

REPORT NO. 2: The kinetics of gaseous-cracking of SiCl_4 and SiHCl_3 in the presence of H_2 to form SiC are discussed. Looped silicon carbide crystals obtained with this method of growth are described and illustrated. An attempt to control nucleation density and growth rate in the solution method by dilution with germanium has been tried and abandoned. The effect of variation of other growth parameters is reviewed. Progress with Hall and resistivity measurements is discussed. Determination of the temperature shift of the optical absorption edge in cubic material is almost complete. Two papers recently given are appended because they summarize the knowledge gained on some of this work to date. Memorandum No. T-237: Crystals of β - SiC have been grown from a melt of semiconductor grade silicon enclosed in a graphite crucible. Temperatures in the 1500° to 2200°C range were used with argon under pressures as high as 800 psi as the ambient. A temperature difference in the range of -15° to 35°C was maintained from top to bottom of the crucible. Carbon from the crucible wall dissolved in the vicinity of the meniscus, diffused to the cooled bottom, and precipitated as dendritic prisms and plates of SiC with (111) and (100) faces predominating. The main function of diffusing a precipitate was to maintain

crucible integrity. The temperature gradient proved important to crystal growth and perfection. Crystals grown by this method were spectroscopically pure, with the exception of approximately 3 parts per million of Ca, Fe, and Mg.

139. Raytheon Manufacturing Co., Waltham, Massachusetts. BETA SILICON CARBIDE. Final Report, 1 December 1959 - 30 November 1960. Warschauer, D. M. 30 January 1961. Report No. S-242, AFCRL-60. (AD-253075). Contract AF 19 (604)-6133.

The work on growing single-crystal silicon carbide in the cubic phase by gaseous cracking of silicon tetrachloride and by growth from elemental silicon fused in a carbon crucible is summarized. Examples of crystals grown by each of these methods are shown. Crystallographic and electrical measurements are treated. Optical data pertinent to the absorption edge and its temperature dependence, as gathered from these samples, are discussed.

140. Royal Aircraft Establishment, Farnborough, Hants, England. PREPARATION OF SINGLE CRYSTALS OF SILICON CARBIDE AND CONTROL OF THE FORM AND AMOUNT OF INCLUDED IMPURITIES. (Darstellung von Einkristallen von Siliciumcarbid und Beherrschung von Art und Menge der Eingebauten Verunreinigungen.) Translated by H. C. Ranson, March 1960. (AD-249685). Translated from German. Library Translation No. 885 of Berichte der Deutschen Keramischen Gesellschaft, J. A. Lely, Vol. 32, pp. 229-231. 1955.

Hexagonal single crystals of SiC were prepared by sublimation of commercial, bright green SiC at 2500° to 2600°C. The resulting crystals are colorless. Inclusion of elements of group 3 in the lattice gave crystals which were blue and showed defective conductivity. Elements of group 5 gave a green color and excess conductivity.

141. Royal Aircraft Establishment, Farnborough, Hants, England. SILICON CARBIDE. A REVIEW. Technical Note No. Met Phys. 325. Brown, A. R. G. August 1960. (AD-249685).

Published information on the production of pure silicon carbide and the fabrication of dense bodies of pure self-bonded SiC is reviewed. The structure and growth mechanism of SiC are briefly considered and the major chemical, physical, and mechanical properties are abstracted.

142. Rücker, D.
THE ELECTROLUMINESCENCE OF SILICON CARBIDE.
Zeitschrift Fuer Angewandte Physik, Vol. 10, No. 6, pp.
254-263. June 1958. (In German).

On application of a field biased in the forward direction across blue SiC crystals (p-type, with n-type surface layer), hole injection occurs at p-n junctions, giving rise to luminescence. Under reverse bias, luminescence due to impact ionization occurs at discrete points in the p-n exhaustion layer of blue crystals, and in the surface exhaustion layer of green crystals (n-type). The maximum of the injection luminescence spectrum lies between 5100 and 6300 Å, shifting to the shorter wavelengths with increasing conductivity and current density and decreasing temperature. The decay time (3-8 microseconds) shortens with increasing current density. The impact luminescence emission extends from the ultraviolet to the red end of the spectrum, with a maximum at 4650 Å; the decay time is less than 2×10^{-7} second.

143. Shashkov, Yu. M. and Shushlebina, N. Ya.
SiC GROWTH FROM Si MELT. Fizika Tverdogo Tela, Vol. 6,
No. 5, pp. 1449-1452. 1964. (In Russian).

The growth of single crystals of β -SiC from a Si melt was studied. The melt was prepared in vacuo in a graphite crucible. Four types of single-crystal SiC are found which are formed in the Si melt. The main-surface which limits the crystals is the (111) surface.

144. Shockley Transistor Corporation, Mountain View, California.
PREPARATION OF SEMICONDUCTOR MATERIALS. Quarterly
Technical Report No. 1, 24 June - 15 December 1957.
Shockley, William. December 1957. (AD-298634).
Contract NObsr-72706.

No abstract.

145. Singh, G. and Verma, A. R.
THE STRUCTURE OF A NEW SILICON CARBIDE POLYTYPE
105R. Acta Crystallographica, Vol. 17, pp. 49-51. January
1964.

The 105-layered rhombohedral polytype of SiC with unit-cell dimensions $a = b = 3.078$ and $c = 264.39$ Å, as referred to hexagonal axes, is discussed. By comparing the calculated relative intensities of 10.1 reflections with those observed on Weissenberg photographs, its structure has been confirmed to be $(33333333332)_3$ in Zhdanov's notation. This polytype belongs to the $|(33)_n 32|_3$ series of structures whose existence is expected on the dislocation theory.

146. Stanford Research Institute, Menlo Park, California.
BETA-SILICON CARBIDE AND ITS POTENTIAL FOR DEVICES.
Quarterly Technical Report No. 1, 1 February - 30 April 1962.
Halden, F. A. and Meuli, W. P. 15 May 1962. Report No. 3.
(AD-276160). Contract NObsr-87235.

Initial measurements of the N content of SiC crystals, grown by the solution technique during the previous program, showed a level of 7.3 by 10 to the 18th power atoms per cubic centimeter. This is closely comparable to the value 2.1 by 10 to the 19th power carriers per cubic centimeter obtained previously from Hall measurements on these crystals. Although additional measurements will be required to ensure the validity of these results, these data appear to confirm that N is the impurity doping these crystals. In considering the sources for N contamination during crystal growth, it appears that N adsorbed on the graphite crucible and subsequently incorporated into the SiC coating is responsible. In view of the gettering action of crystallizing SiC at low temperatures and the fact that the SiC coating acts as the sources of C during crystal growth, it is considered that improvements in the coating technique are essential. For this reason, a Si vapor deposition process was selected to replace the powder application procedure previously employed. With this new process, the crucible can be vacuum-outgassed at a high temperature and repeatedly coated and reacted to form the SiC layer without exposing the crucible to air at any point in the coating process. Pyrolytic graphite is also being evaluated as a high-purity crucible material.

147. Stanford Research Institute, Menlo Park, California.
BETA-SILICON CARBIDE AND ITS POTENTIAL FOR DEVICES.
Quarterly Technical Report No. 2, 1 May - 31 July 1962.
Nelson, W. E. and Halden, F. A. 15 August 1962. Report No. 6. (AD-282636). Contract NObsr-87235.

The first low-nitrogen beta-silicon carbide crystals were grown. Analysis revealed a tenfold decrease in nitrogen contamination compared with crystals grown previously. Electrical measurements of the low-nitrogen crystals (3.4 by 10 to the 17th power atoms per cubic centimeter) showed an order-of-magnitude increase in resistivity to 0.45 ohm-centimeter. Successful crystal growth runs were made in pyrolytic graphite-coated UF-4S graphite crucibles and in purified, high-density graphite crucibles.

148. Stanford Research Institute, Menlo Park, California.
BETA-SILICON CARBIDE AND ITS POTENTIAL FOR DEVICES.
Quarterly Technical Report No. 3, 1 August - 31 October 1962.
Nelson, W. E. 15 November 1962. Report No. 9.
(AD-289015). Contract NObsr-87235.

The resistivities of crystals of beta-SiC grown during this quarter increased nearly another order of magnitude over those obtained during the last report period. This increase from approximately 0.5 to 3.8 ohm-centimeter, accompanied progress in minimizing the sources of N contamination during crystal growth. Routine degassing of graphite crucibles at 2150°C and 10 to the -5th power millimeter of mercury within the crystal grower was achieved. Analyses of Si stock used for crystal growth revealed N contents as high as 43 parts per million. Specially purified low-N-content Si rod was obtained, and a vacuum extraction procedure for removing any remaining dissolved N was developed. Analyses of ordinary standard tank He used for the crystal growing furnace atmosphere revealed N contamination as high as 600 parts per million. Analyzed premium grade He containing less than 10 parts per million N was received from suppliers and a new bakeable purification train is being constructed to ensure an N-free furnace atmosphere.

149. Stanford Research Institute, Menlo Park, California.
BETA-SILICON CARBIDE AND ITS POTENTIAL FOR DEVICES.
Quarterly Technical Report No. 4, 1 November 1962 - 31 January 1963. Nelson, W. E. 15 February 1963. Report No. 12. (AD-297821). Contract NObsr-87235.

No abstract.

150. Stanford Research Institute, Menlo Park, California.
BETA-SILICON CARBIDE AND ITS POTENTIAL FOR DEVICES.
Quarterly Technical Report No. 5, 1 February - 30 April 1963.
Nelson, W. E. and Halden, F. A. 15 May 1963. (AD-405029).
Contract NObsr-87235.

P-type crystals were grown using boron and aluminum additions to the silicon melts. Some difficulty arose as a result of compensation by impurities in the boron employed, but doping levels obtained using aluminum additions appeared quite uniform and amenable to control. Satisfactory results are anticipated for boron when higher purity, zone-refined rod form is used. Ohmic contacts were obtained on low resistivity (0.1 to 1.0 ohm-centimeter) n-type silicon carbide by soldering gold wires directly to the crystals. A number of crystals were prepared for Hall measurements (five-contact method) using this technique. For high resistivity silicon carbide, ohmic contacts were prepared by flash-fusing carbon-saturated silicon on the crystal surfaces in an arc-image furnace. Rectifying contacts were prepared by this technique using carbon-free silicon of the proper conductivity type. Simple diodes were produced from p-type beta-silicon carbide crystals. Intense light was observed at the emitting junction when some of these diodes were being tested.

151. Stanford Research Institute, Menlo Park, California.
GROWTH OF SILICON CARBIDE SINGLE CRYSTALS. Report
No. 37, 15 June 1961. Meuli, W. P. and Fredericks, W. J.
20 June 1963. U. S. Government Research Reports, Vol. 38,
p. 26(A). (AD-298670). Contract NObsr-72772.

No abstract.

152. Stanford Research Institute, Menlo Park, California.
BETA-SILICON CARBIDE AND ITS POTENTIAL FOR DEVICES.
Final Report No. 21, 31 December 1963. Nelson, W. E.,
Halden, F. A., and Rosengreen, A. 20 April 1964. U. S.
Government Research Reports, Vol. 39, p. 32(A).
(AD-428005). Contract NObsr-87235.

No abstract.

153. Sturges, Donald G.
CERAMICS: A NEW DIMENSION IN CIRCUITRY. Electronic Industries, Vol. 22, pp. G15-G16. June 1963.

Brief review of the electronic applications of various ceramic materials. The use of alumina, beryllia, and boron nitride is noted, as is the work on silicon carbide semiconductors, and their application as thermistors, transistors, and high-temperature rectifiers. The use of ceramics in lasers and masers is also noted, as is their employment as electromagnetic windows for space purposes. Ceramic band-pass filters and piezoelectric devices are also considered.

154. Technical Research Group, New York, New York.
DEVELOPMENT OF THE PERIODIC SHOCK WAVE TECHNIQUE AND ITS APPLICATION TO THE PREPARATION OF SEMICONDUCTOR SILICON CARBIDE. Report No. AFCRL TR 58-193, August 1958. (AD-160872).

No abstract.

155. Technical Research Group, New York, New York.
DEVELOPMENT OF THE PERIODIC SHOCK WAVE TECHNIQUE AND ITS APPLICATION TO THE PREPARATION OF SEMICONDUCTOR SILICON CARBIDE. Report No. TRG-117-FR.
Teja, J. Dherma. January 1960. Report No. AFCRC TR 60-105. (AD-240602).

The periodic shock tube has been investigated as a high-temperature device for the pyrolytic decomposition of various organo-silicon compounds into silicon carbide. Temperatures in the range 1100°F were produced in a periodic shock tube (gas-driven jet resonance tube). The results of hundreds of experimental runs show that silicon carbide is obtained in a comparatively impure form in such a shock tube.

156. Texas Instruments, Inc., Dallas, Texas.
SEMICONDUCTOR RESISTIVE ELEMENT. Final Report, 1 July - 31 December 1961. 30 January 1962. (AD-271050). Contract NObsr-85406.

Efforts were made to develop a low temperature coefficient of resistance (TCR) semiconductor resistive element with more stable characteristics and greater reliability than the metal film resistors presently on the market. Several semiconductor

materials (reduced titania, silicon carbide, silicon boride, gallium arsenide, etc.) were considered as bulk elements and for various reasons were rejected. The elements thought most promising were silicon layer configurations formed either by diffusion or by vapor deposition. Silicon layer elements in the preliminary stages of development exhibited TCR's as low as 350 parts per million at resistivities of approximately 0.0X ohm-centimeter. Load life and TCR data are presented for both the standard network devices and the experimental silicon-diffused, epitaxial, and polycrystalline elements.

157. Tomita, T.
CRYSTAL STRUCTURE OF SILICON CARBIDE OF 174 LAYERS.
Journal of the Physical Society of Japan, Vol. 15, pp. 99-105.
January 1960.

A new modification of silicon carbide having rhombohedral symmetry, and a unit cell composed of 174 layers, is reported. The cell size and symmetry were determined by the method employed by Honjo, et al, to study silicon carbide of 594 layers. The structure, namely the stacking order of Si-C layers, of the new modification was determined by comparing the intensity of X-ray reflections with those calculated for a number of models. The structure is represented by $\{C(CCH)_7C_3(CCH)_{11}\}$ times 3 in Wyckoff's notation.

158. Transatron Electronic Corporation, Wakefield, Massachusetts.
THE FABRICATION OF SILICON CARBIDE JUNCTIONS.
Scientific Report No. 1. Hergenrother, Karl M. 5 November 1959. AFCRC TN 59-960. (AD-230546). Contract AF 19 (604)-4989.

It has been found possible to grow p-n junctions in silicon carbide by depositing a single crystal film from the vapor phase onto a silicon carbide seed. The junction is made by adding impurities to the ambient gas in the furnace during the crystal growth. The method for growing such films and controlling the doping is discussed. The calculated electrical characteristics of such junctions compare roughly with those found experimentally. These p-n junctions are suitable for fabricating diodes and other junction devices which will operate at 500°C and have relatively good resistance to high energy radiation.

159. Transitron Electronic Corporation, Wakefield, Massachusetts. THE EPITAXIAL GROWTH OF HEXAGONAL SILICON CARBIDE ONTO SEEDS. Report No. AFCRL TN 60-372. Hergenrother, Karl M. April 1960. (AD-237098).

No abstract.

160. Transitron Electronic Corporation, Wakefield, Massachusetts. METHOD OF PURIFYING SILICON CARBIDE. Hergenrother, Karl M. U. S. Patent 2,996,415 issued 15 August 1961.

A method for removing metallic impurities, especially aluminum, from silicon carbide is described. The silicon carbide is dissolved in a melt of chromium containing oxygen, preferably as an oxide of chromium, and a crystal is grown from the melt. The oxygen reacts with the aluminum at the temperature of the melt-crystal interface and forms an oxide with a high heat of formation, thus removing the aluminum from the silicon carbide. The chromium also removes traces of silicon or carbon impurities in the silicon carbide. Other impurities such as zirconium and titanium can also be removed by forming an oxide with a high heat of formation. Junctions can be formed by controlling the amount of oxygen in the chromium.

161. Transitron Electronic Corporation, Wakefield, Massachusetts. METHOD OF GROWING SILICON CARBIDE CRYSTALS. Hergenrother, Karl M. U. S. Patent 2,996,456 issued 15 August 1961.

The growth of silicon carbide crystals from a melt consisting of silicon carbide dissolved in a solvent such as silicon or chromium is discussed. The crystal may be grown by pulling a silicon carbide seed from the melt or by passing a molten solvent zone through a crystal. In the latter case, a sandwich consisting of a layer of silicon carbide, a layer of chromium, and another layer of silicon carbide is formed and a temperature gradient is applied across the sandwich. The chromium melts and the gradient causes the molten layer to pass through the hotter semiconductor. Silicon carbide crystals are grown on the unmelted layer as the molten zone passes through the sandwich. If both SiC layers are p-type and the molten zone is chromium, the regrown layer is n-type. If both layers are n-type and the chromium is doped with boron, the regrown layer is p-type.

168. Tyco Laboratories, Inc., Waltham, Massachusetts.
THE TRAVELLING SOLVENT METHOD OF CRYSTAL GROWTH.
Quarterly Report No. 6, 16 August - 15 November 1962.
Griffiths, L. B., Wright, M. A., and Mlavsky, A. I. 15
December 1962. AFCRL 62-971. Contract AF 19(604)-8803.

Large crystals of α -SiC have been grown from solution in chromium by the Travelling Solvent Method at an average temperature of approximately 1800°C. The major problem has been the proper wetting of the SiC surface by chromium; this problem has now been solved using an ultrahigh vacuum heating treatment, followed by the evaporation of chromium onto the clean surfaces. Preliminary experiments using silicon and platinum as solvents have shown encouraging results.

169. Tyco Laboratories, Inc., Waltham, Massachusetts.
THE TRAVELLING SOLVENT METHOD OF CRYSTAL GROWTH.
Quarterly Report No. 7, 16 November 1962 - 15 February 1963.
Griffiths, L. B., Wright, M. A., and Mlavsky, A. I.
12 March 1963. AFCRL 63-75. (AD-400993). Contract
AF 19(604)-8803.

Single crystals containing large area p-n junctions have been prepared utilizing the travelling solvent method. Since both p and n conductivity type of SiC were available, sandwiches were assembled so that one type could be deposited from Cr-rich solution onto the other. The darker colored (p-type) material remained transparent following passage of Cr through it. No unsuccessful zone passing experiments were encountered with the new technique. In addition to p-n junction fabrication, using the foregoing method, a few experiments were performed by doping the travelling zone at some point during its passage. A sample, rather dirty, p-type material was used for the test during which nitrogen was added to the usual argon blanket gas. Nitrogen is a well known n-type dopant inducing a level at about 0.03 electron volt below the conduction band.

170. Tyco Laboratories, Inc., Waltham, Massachusetts.
THE TRAVELLING SOLVENT METHOD OF CRYSTAL GROWTH.
U. S. Government Research Reports, Vol. 38, p. 35(A).
Weinstein, M., Wright, M. A., Griffiths, L. B., and Mlavsky,
A. I. 20 December 1963. AFCRL 63-314. (AD-415923).
Contract AF 19(604)-8803.

The growth of single crystals of GaAs and SiC by a Travelling Solvent Method is discussed. The effects of temperature, temperature gradient, zone thickness, and crystal face relationship on crystal growth by Travelling Solvent Method was investigated. Purification of the GaAs crystals and a decrease in dislocation density occurred during crystal growth by Travelling Solvent Method. For GaAs crystal growth from Ga, the process was found to be diffusion controlled. P-n junctions were grown in GaAs by Travelling Solvent Method. These junctions all showed the square law behavior characteristic of an extremely abrupt junction.

171. Union Carbide Corporation, Parma Research Laboratory, Ohio. PROCESS FOR DEPOSITING BETA SILICON CARBIDE. Gareis, Paul J. and Mohr, Paul H. U. S. Patent 3,011,912 issued 5 December 1961.

The process comprises heating a substrate at 750° to 1400°C in a reactant atmosphere of tetramethylsilane, a mixture of tetramethylsilane and methane, or a mixture of silane and methane maintained at a pressure of 0.1 to 2 millimeters of mercury, to deposit a film of β -silicon carbide on the substrate.

172. United Kingdom Atomic Energy Authority, Reactor Group, Risley, Lancs, England. BIBLIOGRAPHY ON THE PRODUCTION AND PROPERTIES OF SILICON CARBIDE. Chadwick, U. R. M. Comp. 20 March 1963.

References (368) are given to books, reports, patents, and journals published from 1948 through August 1962.

173. Violin, E. E. and Kholuyanov, G. F. ELECTRO- AND PHOTOLUMINESCENCE OF DIFFUSIONAL p-n JUNCTIONS IN SiC. Fizika Tverdogo Tela, Vol. 6, No. 6, pp. 1696-1701. 1964. (In Russian).

The structure was considered of electroluminescence and photoluminescence of diffusional p-n junctions in n-SiC of 6H and 4H polytypes. The spectra and temperature dependence of photoluminescence are compared to the initial crystals and p-n junctions. Introduction of B by diffusion leads to the formation of sharp bands of photoluminescence and electroluminescence of p-n junctions, which are not observed in the photoluminescence spectra of the initial crystals.

174. Wacker-Chemie, G. m. b. H.
PROCESS FOR THE MANUFACTURE OF VERY PURE
CRYSTALLINE CARBIDES, NITRIDES, OR BORIDES.
British Patent 968,590 issued 2 September 1964. German
application. 8 October 1959.

Process for the manufacture of very pure crystalline carbides, nitrides, or borides of elements of Groups III-VI, in which the carbide, nitride, or boride to be treated, while adhering to a carrier, is sublimed from the latter by the action of heat in an atmosphere of an inert gas onto a condensation element a fall of 1° to 2000°C from the temperature of the carrier to that of the condensation element being maintained during the sublimation. The carrier may be composed of graphite or the substance to be sublimed, and is conveniently on the outer surface of the material to be treated.

175. Wallace, L. F. and Chang, H. C.
SILICON CARBIDE TRANSISTORS. Journal of the Electrochemical Society, Vol. 107, p. 269(A). December 1960.

High-temperature unipolar transistors exhibiting power gain which use n-type α -SiC for the channel material were described. The p-type gates were formed by the aluminum-diffusion process. The high-purity material was prepared in a Lely-type furnace and has a minimum resistivity of about 500 ohm-centimeters at room temperature. Control of the channel geometry was achieved by diffusion and electrolytic etching techniques. The design principles and electrical characteristics were presented.

176. Warschauer, D. M.
BETA SILICON CARBIDE. PB Report 148354. U. S. Government Research Reports, Vol. 34, No. 4, p. 499. 1960.

The results of tests for the optimum composition of gas for the vapor-decomposition method of growth indicate that best results are achieved when hydrogen and silicon tetrachloride are used alone rather than with the addition of a carbon-bearing compound. The best crystals have been grown at 1950°C; they are stoichiometric to within 0.3 percent, and the impurity content does not exceed 0.003 percent of the most abundant impurity. The formation of methane and of high molecular weight complexes of silicon dichloride are important factors in the growth process. Somewhat smaller crystals of a different shape are being grown

by deposition from solution. Advances have been made in improving the purity of this material, and preliminary measurements of electrical properties are under way.

177. Warschauer, D. M.
BETA SILICON CARBIDE. PB Report 152628. U. S. Government Research Reports, Vol. 35, No. 3, p. 346. 1961.

The kinetics of gaseous cracking of SiCl_4 and SiHCl_3 in the presence of H_2 to form SiC are discussed. Looped silicon carbide crystals obtained with this method of growth are described and illustrated. An attempt to control nucleation density and growth rate in the solution method, by dilution with germanium, was abandoned. The effect of variation of other growth parameters is reviewed. Progress with Hall and resistivity measurements is discussed. Two papers recently given are appended because they summarize the knowledge gained on some of this work to date.

178. Weiszburg, J.
ON THE ELECTROLUMINESCENCE OF INSULATED SiC CRYSTALS. Acta Physica Hungarica, Vol. 11, No. 1, pp. 95-96. 1960 (In Hungarian).

Electroluminescence was observed in crystals of SiC unaccompanied by the usual rectifying effect. The light was emitted when the specimen was separated from one of the electrodes by a mica sheet, requiring an average field of about 10^6 volt centimeter⁻¹ ac or 20 times the field necessary to produce the same color, distribution, and intensity without the mica. This is interpreted as meaning that the electrons causing the light are supplied by surface states rather than by injection from the electrodes, so that SiC electroluminescence can be likened to that of ZnS.

179. Westinghouse Electric Corporation, Boston, Massachusetts.
STUDY, DEVELOPMENT AND APPLICATION OF TECHNIQUES NECESSARY TO FABRICATE ACTIVE SILICON CARBIDE DEVICES. Final Report, 15 August 1959 - 15 October 1960. Chang, Hung-Chi, Wallace, L. Franklin, and LeMay, C. Z. 1 December 1960. AFCRL 107. (AD-250299). Contract AF 19 (604)-5997.

Fundamental techniques were developed for the fabrication of SiC devices in general and unipolar field-effect transistors in particular. The diffusion of Al vapor in alpha-SiC was quantitatively investigated and the diffusion-junction process was developed. Hexagonal SiC was grown in the form of thin platelets which are ready for device fabrication. Device fabrication processes include the single- and double-gate fused junctions, single-gate grown junctions, and single- and double-gate diffused junctions. Only the double-gate diffused junction process produced unipolar transistors which exhibit power gain. These devices are still in a primitive stage of development and will require further development before they become practical devices. An experimental model of a SiC double-gate unipolar transistor was developed that exhibited ac power gain as high as 380 at room temperature and 7 at 500°C.

180. Westinghouse Electric Corporation, Boston, Massachusetts. PREPARATION OF JUNCTIONS IN SILICON CARBIDE MEMBERS. LeMay, C. Z. and Chang, Hung Chi. U. S. Patent 3,063,876 issued 13 November 1962.

The process comprises applying to a single crystal silicon carbide an alloy of 90 to 99.5 Pt, Pd, and/or Rh and 10 to 0.5 percent (weight) doping material to produce a desired semiconductivity in a portion of the silicon carbide and heating the alloy and silicon carbide to produce a molten area of the alloy which dissolves a portion of the contacting silicon carbide.

181. Westinghouse Electric Corporation, Boston, Massachusetts. SURFACE TREATMENT (BY ELECTROLYTIC ETCHING) OF SILICON CARBIDE. Chang, Hung Chi. U. S. Patent 3,078,219 issued 19 February 1963.

No abstract.

182. Westinghouse Electric Corporation, Boston, Massachusetts. THEORETICAL AND EXPERIMENTAL RESEARCH TO ASSIST IN PREPARATION AND DESIGN OF A HIGH FREQUENCY SILICON CARBIDE ACTIVE DEVICE. U. S. Government Research Reports, Vol. 38, p. 35(A). Chang, H. C. 20 July 1963. AFCRL 63-61, December 1962. (AD-402193). Contract AF 19(604)-8499.

A unipolar SiC transistor capable of operation at temperatures in excess of 500°C is discussed. Epitaxial layers were grown on hexagonal SiC seed crystals. The best layers possess a high degree of crystalline perfection and are quite pure. A study of the diffusion technique showed that by varying the various diffusion parameters, the usual complementary error function behavior of the diffusion front was changed. A gaseous etching technique is described which produces etched surfaces with a uniformity and smoothness previously unattainable. When used in conjunction with various masking techniques, this method appears to be feasible in the production of an active device structure.

183. Westinghouse Electric Corporation, Dayton, Ohio.
RESEARCH ON SILICON CARBIDE TRANSISTORS. Scientific
Report No. 1, 15 April - 15 July 1958. (AD-208461).
Contract AF 33(616)-5592.

Theoretical analyses were made for an NPN transistor. The base width of a practical device should be in the order of 1 micron if the electron lifetime is within the range of 0.01 to 0.01 microsecond. The field-effect transistor is more feasible since its operation does not depend upon the minority carrier lifetime. Design nomographs were prepared for the Shockley-type field-effect transistor. Progress has been made on the fabrication techniques. Molten sodium peroxide is a satisfactory preetchant. Electrolytic etching in alcohol solutions of HF is an effective postetching method. Ohmic contacts and fused junctions can be prepared with silicon, platinum, or tungsten alloys, but the breakdown voltage is, in general, lower than grown junctions at the present state-of-the-art. Attempts are being made to design and construct a prototype field-effect transistor. The major difficulty is to obtain crystals of high perfection and to produce junctions of very low leakage current.

184. Westinghouse Electric Corporation, Dayton, Ohio.
RESEARCH ON SILICON CARBIDE TRANSISTORS. Scientific
Report No. 2, 15 July - 15 October 1958. (AD-214955).
Contract AF 33(616)-5592.

Further studies were made on fabrication techniques, such as surface treatment, fusion, and diffusion. Work was emphasized on the preparation of low-leakage junctions and low-resistance contacts. An open-tube carrier-gas method is being developed for vapor diffusion. This method improves the stability of the

crystal surface during diffusion at above 1800°C. The alloy-diffusion method was found promising for forming low-leakage, shallow junctions. Progress was made on fused junctions by improving the alloy composition and thermal conditions.

185. Westinghouse Electric Corporation, Dayton, Ohio.
RESEARCH ON SILICON CARBIDE TRANSISTORS. Scientific
Report No. 3, 15 October 1958 - 15 January 1959.
(AD-219189). Contract AF 33(616)-5592.

Measuring equipment was constructed which could be used on any three-terminal amplifier to measure both dc and ac input and output characteristics. Diffused junctions were made using n-type α -SiC crystals and a carrier gas with aluminum as the doping impurity. Reverse voltages up to 200 volts have been obtained. Preliminary work was done toward fabricating these junctions into field-effect transistors. Order-of-magnitude values for the diffusion constant of aluminum into silicon carbide were found to be 5×10^{-11} square centimeters per second at 2050°C and 3.5×10^{-12} square centimeters per second at 1850°C. Alloy-diffused junctions were consistently produced which had reverse breakdown voltages greater than 100 volts.

186. Westinghouse Electric Corporation, Boston, Massachusetts.
RESEARCH ON SILICON CARBIDE TRANSISTORS. Scientific
Report No. 4, (Summary) 15 January - 15 July 1959.
AFCRC TN 59-951. (AD-230083). Contract AF 33(616)-5592.

Further progress has been made on fusion and diffusion techniques. The boron-tin-platinum alloy was found to be the most promising one for forming p-n junctions in n-type silicon carbide. The rectification ratios for the fused junctions were higher for higher fusion temperature and greater temperature gradient normal to the regrowth layer. The highest reverse voltage obtained was 400 volts. The diffusion of aluminum in α -SiC in the [0001] direction has been measured in the temperature range of 1750° to 2000°C. These diffusion constants can be expressed by the equation $D(T) = 1.8 \exp(-13,000/RT)$ square centimeters per second. The advanced fusion techniques have been employed to fabricate unipolar field-effect transistor structures from fused and grown junction crystals. A unit with ac power gain has not yet been constructed.

187. Westinghouse Electric Corporation, Dayton, Ohio.
500°C SILICON CARBIDE RECTIFIER PROGRAM. U. S.
Government Research Reports, Vol. 37, p. 19(A), 20 August
1962. Chang, H. C., Campbell, R. B., et al. April 1962.
ASD TR 7-727(2). (AD-275540). Contract AF 33(657)-7027.

Hexagonal SiC crystals have been grown in a Kroll-type furnace by the sublimation technique. The research on grown junction crystals emphasized the determination of conditions for the preparation of crystals with a high degree of surface and internal perfection and of sufficient size to carry the required current. Al-diffusion experiments resulted in junctions with milli-ampere current carrying capacity. Methods and materials of device fabrication were studied and revised to meet the specification of vacuum-tight operation for 1000 hours at 500°C. Electrical characteristics are given for an exceptional encapsulated rectifier at 300°, 400°, and 500°C.

188. Westinghouse Electric Corporation, Dayton, Ohio.
500°C SILICON CARBIDE RECTIFIER PROGRAM. Interim
Technical Progress Report No. 3, 1 April - 31 June 1962.
Chang, H. C., Campbell, R. B., et al. July 1962. ASD TR
7-727, Vol. 3. (AD-283660). Contract AF 33(657)-7027.

Silicon carbide crystals of the hexagonal type were grown in a Kroll-type furnace by the sublimation technique. Both homogeneous and grown-junction crystals were prepared. To increase the yield and quality of the grown crystals, a new Kroll-type furnace was constructed and is being tested. The feasibility of vapor-phase chemical reaction methods was investigated for the controlled growth of silicon carbide platelets and sheets. The growth of junction crystals has emphasized the preparation of crystals with a high degree of perfection. The methods of rectifier fabrication are being studied. An improved metal ceramic header was tested and found to remain vacuum-tight after operation at 500°C. The characteristics of two 1-ampere rectifiers and a group of low-current rectifiers are discussed.

189. Westinghouse Electric Corporation, Dayton, Ohio.
500°C SILICON CARBIDE RECTIFIER PROGRAM. Interim
Technical Progress Report No. 4, 1 July - 30 September 1962.
Chang, H. C., Campbell, R. B., et al. October 1962. ASD
TR 8-828, Vol. 4. (AD-288262). Contract AF 33(657)-7027.

Silicon carbide crystals of the hexagonal type were grown in a Kroll-type furnace by the sublimation technique. Both homogeneous and grown-junction crystals were prepared. A new Kroll-type furnace was constructed. Preliminary runs were made, yielding crystals of high purity. The growth of junction crystals has emphasized the preparation of crystals with a high degree of perfection. The methods and materials of rectifier fabrication are being studied. Ambient effects and electrical characteristics of three rectifiers are given.

190. Westinghouse Electric Corporation, Dayton, Ohio.
500°C SILICON CARBIDE RECTIFIER PROGRAM. Interim Technical Progress Report No. 5, 1 October - 31 December 1962. Chang, H. C., Campbell, R. B., et al. January 1963. ASD TR 7-727, Vol. 5. (AD-296942). Contract AF 33(657)-7027.

Hexagonal silicon carbide crystals are being grown in a kroll-type furnace by the sublimation technique. In order to obtain greater control over the growth variables, a new furnace has been assembled and is being used in a series of experiments. This furnace should give valuable information on crystal growth parameters. The research on grown-junction crystals has emphasized the preparation of crystals with a high degree of surface and internal perfection by studying the effect of radiation sinks and cavity geometry. The methods and materials of device fabrication are being studied and adapted to meet stability and quantity processing requirements. Electrical characteristics at various temperatures are given for several encapsulated rectifiers. The electrical properties of these rectifiers had been stabilized by an ambient atmosphere treatment prior to encapsulation.

191. Westinghouse Electric Corporation, Dayton, Ohio.
500°C SILICON CARBIDE RECTIFIER PROGRAM COVERING PERIOD 1 JANUARY TO 31 MARCH 1963. Interim Technical Progress Report No. 6, 31 March 1963. ASD TR 7-727, Vol. 6. (AD-405752). Contract AF 33(657)-7027.

Efforts were continued on the production of 500°C silicon carbide rectifiers. The effects of different-sized cavities were investigated in the standard sublimation furnace. It was found that larger cavities greatly affect growth conditions and, under normal circumstances, little is gained by changing cavity geometry. Different heat sinks produced an effect on the

crystal growth, but there was no significant effect on the increase of yield. Epitaxial growth of thin SiC layers of both p- and n-type was achieved on silicon carbide substrates. Small area epitaxial rectifiers are being prepared for evaluation. A simplified passivation technique was developed for the 1-ampere rectifier.

192. Westinghouse Electric Corporation, Youngwood, Pennsylvania. 500°C SILICON CARBIDE RECTIFIER PROGRAM. Technical Progress Report No. 8, 1 July - 30 September 1963. Chang, H. C., Jennings, V. J., Thornburg, D. R., Kroko, L. J., Ostroski, J., et al. ASD IR 7-727(VIII). (AD-420375). Contract AF 33(657)-7027.

The growth rate of silicon carbide crystals prepared by the sublimation method has been determined by measuring the amount of growth between successive timed-dopant additions. This has been compared with the growth rate as obtained from a simple model. All values agree within a factor of five. The use of molten borax as an etchant for silicon carbide has been studied. Due to its relatively slow etch rate (about 30 times slower than a molten sodium peroxide-sodium hydroxide mixture) a much finer control of the etching is possible. Details are given on the life and storage tests that were successfully passed by two silicon carbide rectifiers. An open-tube flowing gas system has been shown suitable for the surface passivation of groups of silicon carbide rectifiers.

193. Westinghouse Research Laboratories, Pittsburgh, Pennsylvania. 500°C SILICON CARBIDE RECTIFIER PROGRAM. Interim Technical Progress Report No. 10, 1 January - 31 March 1964. Chang, H. C., Thornburg, D. R., Roach, C. J., Ostroski, J., and Barrett, D. L. April 1964. (AD-601008). Contract AF 33(657)-7027.

The various stations of a pilot line are described. As much of the processing as possible is done in controlled atmosphere dry boxes. The design of the new sublimation furnace was completed and it is being fabricated. Further development work is being carried out on the crystal growth phase of the program. With the addition of graphite felt to the furnace as an insulating material, pump downtime was materially reduced. Progress is being made on the solid doping technique for aluminum and p and n type junctions are being grown.

194. Westinghouse Electric Corporation, Dayton, Ohio.
SILICON CARBIDE, 500°C POWER RECTIFIERS. Interim
Engineering Report No. 1, 25 June - 30 September 1962.
Chang, H. C. and Campbell, R. B. (AD-297975). Contract
AF 33(657)-8719.

This report concerns progress on the growth of semiconductor grade silicon carbide crystals and the preparation of large area junctions for use in the fabrication of power rectifiers.

The various methods which have been used for the preparation of silicon carbide crystals have not resulted in material of sufficient size, purity, and perfection to be used for power rectifiers with ratings of the order of 10 amperes. The main efforts of the present program are studies of new techniques of crystal growth and junction formation and improvements in previous techniques which may lead to the production of silicon carbide crystals with the required properties.

Thus far the work has emphasized the initial experiments on a Kroll-type sublimation furnace of improved design. With this furnace, attempts are being made to grow crystals of larger size and a higher purity than has heretofore been possible. The crystals obtained in the first runs have been of high purity. Initial problems concerning the power supply and cooling system have been solved by using a small amount of powdered insulation adjacent to the heater.

Fabrication has been started on a design of a modified Czochralski apparatus. With this apparatus, experiments on pulling a seed crystal out of a supersaturated vapor will be started. The major difficulty with this method will be very slow rate of growth. Also, the introduction of the seed crystal and the pulling rod will have an effect on the temperature and temperature gradient.

The methods of large-area junction preparation include diffusion and epitaxially grown layers. These processes are in a preliminary stage of investigation.

195. Westinghouse Electric Corporation, Dayton, Ohio.
SILICON CARBIDE, 500°C POWER RECTIFIERS. Interim
Engineering Report No. 3, 1 January - 31 March 1963.
Chang, H. C., Campbell, R. G., Jennings, V. J., and
Sommer, A. (AD-410266). Contract AF 33(657)-8719.

Notice: No automatic release to foreign nationals.

Research was continued on a study of methods and processes suitable for the preparation of semiconductor grade silicon carbide crystals for use in the fabrication of power rectifiers. Progress is presented on the growth of semiconductor grade silicon carbide crystals and the preparation of large-area junctions for use in the fabrication of power rectifiers. The vapor growth of large and pure silicon carbide crystals, using the new sublimation furnace, was achieved. Much optimization work is necessary, however, to obtain crystals suitable for device fabrication. Neither the vapor phase-thermal reduction nor the modified Czochralski techniques has produced elongated crystals although subsidiary information of value has been obtained. The process of epitaxially growing SiC on a single-crystal SiC platelet has been shown feasible, although X-ray evidence has shown that the type and perfection of the substrate is of paramount importance. Dopants added to the reaction do not appear to adversely affect the structure of the grown layer.

196. Westinghouse Electric Corporation, Dayton, Ohio.
SILICON CARBIDE, 500°C POWER RECTIFIERS. Interim Engineering Report No. 4, 1 April - 30 June 1963. Chang, H. C., Campbell, R. G., Jennings, V. J., Kroko, L. J., and Sommer, A. (AD-413163). Contract AF 33(657)-8719.

Notice: No automatic release to foreign nationals.

This report concerns progress on the growth of semiconductor grade silicon carbide crystals, and on several methods used for the preparation of large-area junctions. Thus far, the sublimation method has been most successful in preparing the large-sized crystals needed for power rectifier fabrication. The epitaxial growth method has been utilized to prepare both n-type and p-type doped layers. X-ray studies have shown a high degree of correlation between the substrates used for the epitaxial growth and the subsequent grown layers. Initial studies have begun on the diffusion of boron into SiC.

197. Westinghouse Electric Corporation, Pittsburgh, Pennsylvania.
THEORETICAL AND EXPERIMENTAL RESEARCH TO ASSIST IN PREPARATION AND DESIGN OF A HIGH FREQUENCY SILICON CARBIDE ACTIVE DEVICE. Scientific Report No. 1 and 2. Chang, H. C. January 1962. AFCRL 62-73.
Contract AF 19(604)-8499.

The large band gap of silicon carbide makes it an interesting material for use in semiconductor devices which are operable at ambient temperatures in excess of 500°C. It has been shown that silicon carbide has a higher tolerance to radiation damage than silicon. The objective of the present program is a theoretical and experimental investigation of a high-frequency silicon carbide transistor operable at 500°C, prepared by vapor-phase epitaxial growth techniques. The main advantage of the epitaxial growth method is the precise control obtainable over the junction structure. An apparatus for investigating epitaxial growth by the thermal reduction of silicon and carbon compounds has been constructed. Preliminary results indicate that growth has taken place although this growth shows structural defects. Junctions formed by this technique have shown rectifying properties. A diffusion process is being used as a supplementary method to prepare the junctions necessary for the high-frequency transistor. Diffused junction crystals have been prepared for evaluation.

198. Westinghouse Electric Corporation, Pittsburgh, Pennsylvania. THEORETICAL AND EXPERIMENTAL RESEARCH TO ASSIST IN PREPARATION AND DESIGN OF A HIGH FREQUENCY SILICON CARBIDE ACTIVE DEVICE. Scientific Report No. 3. Chang, H. C. April 1962. AFCRL 62-335. Contract AF 19 (604)-8499.

The fabrication of a high-frequency silicon carbide transistor requires precise control of junction depths and doping and device configurations. An experimental investigation is being undertaken to adapt the techniques used for the fabrication of silicon transistors to silicon carbide. The techniques under investigation are epitaxial growth, diffusion, and etching and evaporated alloyed contacts. Results of epitaxial growth experiments have been improved by modifications in the apparatus and by varying the experimental conditions, in particular, the substrate temperature and the growth rate. A two-step aluminum diffusion process has been initiated in an attempt to improve the control of the diffused junction properties. Gold-tantalum and gold-tantalum-aluminum have been evaporated on and alloyed with good wetting into silicon carbide. A number of masking materials have been examined and the most promising has been zirconium.

199. Westinghouse Electric Corporation, Pittsburgh, Pennsylvania. THEORETICAL AND EXPERIMENTAL RESEARCH TO ASSIST IN PREPARATION AND DESIGN OF A HIGH FREQUENCY SILICON CARBIDE ACTIVE DEVICE. Final Report. Chang, H. C. December 1962. AFCRL 62-61. Contract AF 19(604)-8499.

For an active device to be usable at temperatures in excess of 500°C, it is necessary that the base material have a large band gap. Of the presently known semiconductors, silicon carbide appears to be the most feasible material for use as a high-frequency device capable of operation at elevated temperatures. A unipolar transistor structure has been investigated, since a field-effect device most nearly fits the peculiar capabilities of silicon carbide. The device requirements are stringent and require a large degree of control over the crystal junction structure. This control is best effected by the epitaxial growth technique. An epitaxial growth reactor has been fabricated and epitaxial layers have been grown on hexagonal silicon carbide seed crystals. The best layers have been shown to possess a high degree of crystalline perfection and are quite pure.

200. Westinghouse Electric Corporation, Pittsburgh, Pennsylvania. SURFACE TREATMENT OF SILICON CARBIDE. Chang, Hung Chi. U. S. Patent 3,078,219 issued 19 February 1962.

This invention relates to the treatment of a surface of crystalline silicon carbide (SiC), and particularly to methods of treating the surface, or a portion thereof, of a single crystal of silicon carbide that may be a part of a fabricated semiconductor device.

201. Westinghouse Electric Corporation, Pittsburgh, Pennsylvania. MINIATURE NEUTRON DETECTOR DEVELOPMENT. Quarterly Progress Report, 1 July-30 September 1963. Weisman, J., editor. 16 October 1963. Work performed under Joint United States - Euratom Research and Development Program. Contract AT(30-1)-2827.

In order to increase radiation lifetime, configurations capable of withstanding 1200° to 1300°C are being developed. Such temperatures should allow substantial annealing of radiation damage. The prime difficulty is the formation of high-temperature contacts. To this end, the techniques for bonding

W to SiC are investigated. Bonds that can withstand a number of thermal cycles are made, but there are a number of voids at the interface. The yield of good counting diodes is satisfactory. Nearly all diodes produced can count a particles. The single most important factor in the production of good counting devices appears to be crystalline perfection. Two diodes contained in vanadium caps are prepared for inpile irradiation studies.

202. Westinghouse Electric Corporation, Youngwood, Pennsylvania. POWER RECTIFIER DEVELOPMENT PROGRAM. Report No. 34953-SR-1. Kroko, L. J. 9 August 1957. Contract AF 33 (600)-34953.

Consideration of the various semiconductor materials for which data are available indicates that gallium phosphide is the logical material to supplement the work on silicon carbide. The preparation of this material has begun and some poor quality material has been made. Rectification at room temperature has been observed with both pressure and alloyed contacts. Experiments are underway to determine the stability of this compound at elevated temperatures. Application of diode theory to gallium phosphide and silicon carbide indicates that both materials are suitable at junction temperatures of 650°C. Silicon carbide grown-junction rectifiers have been shown to rectify at 700°C and, at that temperature, one unit had a leakage of 10 milliamperes at 50 volts.

203. Westinghouse Electric Corporation, Youngwood, Pennsylvania. POWER RECTIFIER DEVELOPMENT PROGRAM. Report No. 34953-SR-2. Kroko, L. J. 7 November 1957. Contract AF 33(600)-34953.

Silicon carbide grown-junctions have shown to rectify at temperatures up to 700°C. The reverse voltage and leakage currents meet the requirements of the contract. This report primarily describes the efforts toward producing a good electrical and mechanical structure for subsequent encapsulation. This includes both etching and contact studies. Additional work has also been done on the production of junctions by fusion and alloying. Polycrystalline gallium phosphide has been prepared by zone refining techniques and point contact rectification has been observed with this material. Attempts to produce fused junctions by polycrystalline gallium phosphide have been unsuccessful.

204. Westinghouse Electric Corporation, Youngwood, Pennsylvania. POWER RECTIFIER DEVELOPMENT PROGRAM. Report No. 34953-SR-5. 31 July 1958. Contract AF 33(600)-34953.

The Power Rectifier Development Program consists of parallel efforts on silicon carbide and gallium phosphide. The work on the development of silicon carbide rectifiers is discussed. This work consists of an investigation of the techniques for making grown junctions and the techniques for making rectifiers from the grown junctions. The preparation of gallium phosphide is discussed. This consists of investigations of zone refining of gallium phosphide, the purification of phosphorus, and the preparation of single crystals of gallium phosphide. Techniques for making rectifiers from gallium phosphide are also discussed.

205. Westinghouse Electric Corporation, Youngwood, Pennsylvania. POWER RECTIFIER DEVELOPMENT PROGRAM. Scientific Report No. 6, 1 August 1958 - 30 April 1959. May 1959. (AD-216282). Contract AF 33(600)-34953.

The high-temperature power rectifier program has consisted of parallel efforts on silicon carbide and gallium phosphide devices. Silicon carbide rectifiers are discussed. A technique was developed suitable for fabrication of 0.5-ampere, 75-volt rectifiers. Preparation of gallium phosphide is discussed. Techniques for making rectifiers from gallium phosphide are discussed.

206. Westinghouse Electric Corporation, Youngwood, Pennsylvania. POWER RECTIFIER DEVELOPMENT PROGRAM. Scientific Report No. 7. Quarterly Progress Report, 1 May - 31 July 1959. August 1959. (AD-225760). Contract AF 33(600)-34953.

The high-temperature power rectifier program was pursued with two different semiconductors. The fabrication of 0.5-ampere, 75-volt rectifiers from silicon carbide is discussed, and the preparation and purification of gallium phosphide is reported. Gallium phosphide rectifier development was temporarily suspended until the material is improved.

207. Westinghouse Electric Corporation, Youngwood, Pennsylvania. POWER RECTIFIER DEVELOPMENT PROGRAM. Report on Flight Vehicle Power, March 1960. WADD TR 59-11. (AD-237402). Contract AF 33(600)-34953.

Notice: Not releasable to foreign nationals.

Completely encapsulated silicon carbide power rectifiers have been developed for high-temperature operation. The junctions are made by controlled doping during the vapor growth of α -SiC single crystals. High-temperature, low-resistance ohmic contacts have been developed which permit operation of these rectifiers at 3 amperes peak forward current and 150 volts peak reverse voltage at an ambient temperature of 500°C. Parallel development of gallium phosphide has yielded material of greater purity and larger crystalline size than previously reported. Gallium phosphide has been made and refined by zone refining, vapor growth, and dilute solution methods. Small-area rectifiers have been made which have a peak reverse voltage of 150 volts and pass 100 milliamperes average current in the forward direction.

208. Westinghouse Electric Corporation, Youngwood, Pennsylvania. RESEARCH IN THE PREPARATION OF HYPERPURE SINGLE CRYSTAL SILICON CARBIDE. Final Report, February 1957 - June 1959. Hamilton, D. R., Chu, T. L., et al. April 1960. AFCRL TR 60-368. (AD-250119). Contract AF 19(604)-2174.

The work is concerned with the preparation of SiC crystals of highest purity. While the technique used is basically that of Lely, much of the work is concerned with the methods by which the overall purity has been increased at least an order of magnitude. Pure SiC now means reproducible samples of thousands to hundreds of thousands ohm-centimeter resistivity (room temperature), with impurity levels of the order of 10 to the 16th power atoms per cubic centimeter. Hall measurements indicate that the density of electrically active levels may be as low as 10 to the 14th power per cubic centimeter. The overall morphology of samples prepared in the laboratory is described. A section is devoted to the origin of screw dislocations which have played such a prominent role in recent studies of spiral growth steps on SiC surfaces, while other samples are shown to be atomically flat. Preliminary studies with the plasmajet have demonstrated its suitability for high-temperature reaction studies.

209. Whitney, E. Dow.
POLYMORPHISM IN SiC. Nature, Vol. 199, No. 4890. 1963.

The activation energy for the transformation of the cubic β -form of SiC into the hexagonal form is derived as 158 kilocalories per molecular weight. Comparison with the total heat of vaporization leads to the conclusion that polymorphism in SiC may be interpreted as proceeding through the vapor phase.

210. Woodbury, H. H. and Ludwig, G. W.
ELECTRON SPIN RESONANCE STUDIES IN SiC. Physical Review, Vol. 124, pp. 1083-1089. 15 November 1961.

Electron spin resonance studies on boron and nitrogen, as impurities in 6H silicon carbide, are discussed. It is concluded that both impurities substitute for carbon and that they occupy the three nonequivalent carbon sites with equal probability. Hyperfine structure is well resolved for both species. The pattern for boron occupying one site is unusual in that the hyperfine splitting vanishes when the applied field is about 50 degrees from the hexagonal axis of the crystal. The nitrogen hyperfine structure is interpretable in terms of some character for the unpaired electron, while the boron hyperfine structure indicates predominantly p character.

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| 13. ABSTRACT This state-of-the-art survey on silicon carbide for semiconductors includes a bibliography of the most important references published as of the end of 1964. The various methods used for growing silicon carbide single crystals are reviewed, as well as their properties and devices fabricated from them. The fact that the state-of-the-art of silicon carbide semiconductors is not further advanced may be attributed to the difficulties of growing single crystals of sufficient size and purity for semiconductor applications. Of the various methods of growing silicon carbide, growth by sublimation appears to be the most successful method. There is considerable variation in the properties of silicon carbide as reported in the literature, mainly because most measurements were conducted on crystals with varying amounts and types of impurities. In the area of devices, rectifiers capable of 500°C operation and unipolar transistors exhibiting power gain at temperatures greater than 500°C have been fabricated. Other devices which have received attention include diodes, photoelectric and electroluminescent devices, and electron emission components. | | |

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